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78/15/9

SIGNIFICANCE OF STEAM PERMITTIVITY OF BUILDING MATERIALS FOR PRESERVATION OF MURALS

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SIGNIFICANCE OF STEAM PERMITTIVITY OF BUILDING MATERIALS FOR PRESERVATION OF MURALS

Irina A. Kuleshova

The preservation of painting in monuments of architecture depends much on the temperature-dampness regime of the constructions (brick or stone walls, stucco layer). The regime, in its turn, depends on general climate conditions, air pollution, level of subsoil waters and content of salts in them, the degree of salting of the building materials and especially the temperature-dampness regime in the building.

While studying the reasons of the destruction of monumental painting it should always be borne in mind that most of the destructions of stucco and layer of paint is due to fluid moisture, ice or water steam.

Up to date the problem related to the constant flow of water near the walls of unheated monuments still remains. The situation is somewhat different with the temperature-dampness regime in the heated buildings. Unfortunately, the problem of limiting variations in the relative humidity of air and its temperature in the monuments of architecture with murals still remains unsolved.

One of the most important items of normalization of temperature and humidity inside the monuments and

the main condition of preserving the monumental painting is the investigation of building materials and the adequate application of restoration materials in each monument to fit the conditions and type of the materials.

In accordance with mordern views, the sorbtion characteristics and the structure of pores in building materials influence ,to a large extent, the process of thermo- and mass-transference in the walls, frost-resistance stability in the aggressive media, water permittivity, intensive absorbtion and release of humidity, deformation, creeping, shrinkage and swelling. Therefore, in spite of the difference in the methods of production and minerological content of building materials their durability and thermo-physical properties are determined mainly by the porous structure of the materials.

To solve the problem of preservation of the monumental painting is impossible without solving a problem of durability of walls (masonry and stucco). The question of retaining the original stucco is the most important in the effort to preserve ancient Russian murals. Very often it is considered that to use good and durable cement mortar for coating and side covering is enough. But, unfortunately, it is not so. The approach to this problem should be very careful

and thorough. It is not only a question of technical means and ways to fix stucco in ordinary buildings but it is a problem of conservation and salvation of wall stucco with unique ancient painting.

Stucco is inseparable of the wall, that is why the "life"of stucco for many centuries depends on the "life" of the wall.

Primarily, various deformations in the wall take place and it should be taken into consideration while choosing the way of stucco fixation. At present this point is being given adequate attention to. What is much worse is the problem of studying such properties as air and steam permittivity, thermoconductivity of a wall etc.

If a certain difference in air pressure is formed on the surface of materials or constructions, the air moves from the area of high pressure to the area of low pressure. i.e. air infiltration occurs. Air permittivity depends first of all on the size and shape of pores and gaps, on the degree of opening and closing of pores and gaps and it is lowered with the increase of humidity. Due to the air permittivity of the walls natural ventilation of the walls themselves occurs. This ventilation facilitates release of humid air accumulated in the pores of the walls and it makes them dry and less thermoconductive.

The stucco layer on the wall greatly reduces its air permittivity. Thus, for example, one-side limestone stucco reduces air permittivity of bricks by 15-20 times, two-side - by 40 times. Cement and sand mortars have air permittivity 50-100 times lower than limestone and sand.

These data, due to general conditions of natural ventilation of the walls, clearly testify to the fact that in certain monuments where full or partial coating of the external wall with cement-sand mortar was applied the murals become rapidly damaged and destroyed.

Water steam of the premises touching the wall is being diffused through its pores into the atmosphere, i.e. in the opposite direction of the outside air. The wonderful peculiarity of the brick wall coated with limestone-sand mortar is the fact that no humidity accumulates in it. If we apply cement substance for coating and after lumping it is less steam permeable than the original stucco and wall, we shall inevitably destroy the painting by fixing the stucco and blocking natural ventilation. If steam permittivity of the wall is low the water steam will be easily condensed on the inner surface (colder than air temperature) of the external wall, and be absorbed by its pores and accumulated in the wall.

Besides, the mortar (stucco) having low steam permittivity has always high thermoconductivity and tiny pores which can absorb water according to the laws of capillarity from the surrounding atmosphere (soil, air, rain or snow). The pores can hold water tightly and conduct it to large distances.

It often happens that restoration materials cause the condensation of humidity if they are more hygroscopic than those of the monument itself. For instance, the injection of plaster for the fixation of limestone and sand layer on masonry etc.

All the breaches of steam permittivity of the wall during restoration lead to the destruction of building materials of the monument and to the formation of salty spots on the surface of the painting. Different biodestructive organisms appear and temperature and power tension is developing on the borderline of the original stucco and restoration insertion. And at last it leads to the destruction of murals in spite of all the artists' attempts to fix the layer of paint and author's stucco.

During recent years the hydrophilous mixtures are actively used for the protection of walls from the condensed humidity. After treating the surface of hydrophilic material with hydrophobic colloids the surface layer of the material becomes waterproof.

Besides, the treatment with hydrophobic substances does not influence the steam and air permittivity of the wall. In this respect the hydrophobic treatment of both the facade walls of the monument and the mural painting has a positive effect.

When hydrophobilized, the material changes the properties of its pores and capillars. The capillar the walls of which have hydrophilic properties the water surface is concave; the capillar with hydrophobic walls the water surface is convex, i.e. the negative capillar pressure will predominate in the hydrophobic materials which prevents the capillar sucking in of water by the material.

It should be noted, however, that hydrophobic treatment of the monument's walls with frescoes should be done very cautiously. If the subsoil waters rise to some level in the walls the hydrophobization is forbidden in this zone as water cannot come out of the masonry to the surface because of the hydrophobic properties of the surface layer of the wall. In this case hydrophobization aggravates the state of the wall, reduces the moisture evaporation from its surface and raises the level of subsoil waters.

The hydroisolation of the foundations of the ancient monuments of architecture solves the problem.

This point is the essential for normalization of temperature-dampness regime of the monument and, unfortunately, has not been settled yet.

In conclusion it should be pointed out that the unique ancient painting will be preserved for long only if normal temperature-dampness regime is observed and the materials for restoration are chosen adequately with regard to physical and mechanical properties and especially steam and air permittivity. Only in this case our descendants will have a chance to see the wonderful mural painting.

78/15/10

PROBLEMS OF PRESERVATION OF MURALS OF ANDREI RUBLEV IN THE ASSUMPTION CATHEDRAL AT VLADIMIR

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PROBLEMS OF PRESERVATION OF MURALS OF ANDREI RUBLEV IN THE ASSUMPTION CATHEDRAL AT VLADIMIR

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The unique frescoes of 1408 painted by Andrei Rublev and Daniel Chorny in the Assumption Cathedral of the 12th century, which are 500 years old, have been time and again renewed, whitewashed and oil-painted. The uncovering of the frescoes from under the latest layers began in the second half of the 19th century when academician Solntsev succeeded in uncovering oil frescoes with the composition "Abraham's Bosom" from under the oil decorations of the 18th century.[1/]

The first thorough and purposeful search of ancient fragments was held in 1882 on the initiative of the Moscow Archeological society under I.E.Zabelin. Compositions "Descent of Holy Ghost", "Transfiguration", "Baptism", "Sacrifice of Ioachim and Anna", "The Entrance into the Temple", "Doomsday" etc. were uncovered from under many oil and lime layers[2/]. Water-colour copies which are now considered to be very valuable historic relics were made from all the uncovered ancient

1/ N.N.Ushakov, Guide through ancient Vladimir and the towns of the Vladimir province, 1913, p.53.

2/ A.Vinogradov. The History of the Assumption Cathedral in the provintial town of Vladimir. Vladimir, 1905, p.87.

fragments by the craftsmen of the Safonov-artel under the supervision of I.E.Zabelin[3/].

It was found during the last restoration work that part of the registered ancient fragments was removed by the Safonov artel. It might have been those fragments whose stucco coating did not hold well on the masonry. Besides, the layer of paint of the fragments in the upper parts of the Cathedral, when prepared for the renovation of the fresco, was thoroughly pumiced. To preserve the original outline of the painting it was necessary to graph it on the wet plaster. All the uncovered and thus treated fragments were painted in distemper in terms of the ancient style. The first scientific treatment of frescoes was carried out in 1918 under the supervision of I.E.Grabar, when the remains of the oil image of the "Doomsday" left by Safonov and also his distemper renovations were removed.[4/]

Within the period from 1918 to 1962 the murals of Andrei Rublev uncovered in 1918 in the back part of the Cathedral were restored many times. These were "Doomsday" in the niches and on the columns under the galleries, "The Annunciation of Zakharij","Angel

3/ They are preserved in the stocks of the Vladimir museum

4/ I.E.Grabar. Ancient Russian Art. M.1966,p.128.

leading the child Forerunner" and other wall paintings on the Northern wall of the credence. In the process of work gum and casein glue were used to fix the layer of paint. The latter has a high coefficient of shrinkage as a result of which the layer of paint began to come off, crack, peel off and fall. The irregular temperature and dampness regime also led to this destruction. By 1968 a special comission found the murals to be an accident risk. To combat the downfall the RSFSR Ministry of Culture entrusted the restorers of the Vladimir Experimental scientific restorstion workshop to carry out a series of research to study the painting and its state and by experimental work make a choice of material and methods of fixing the murals. The supervisors of the work were to be V.V.Filatov,master of Arts and A.V.Ivanov, the engineer-chemist of the All-Union Restoration Institute.

A number of highly durable and stable materials were chosen for the experimental work. As a result, were recommended:water dispersion co-polymers of vinyl acetat with 2-ethylhexylacrylate(VA-2EHA) and with ethyl(SVED) and silicon organic resins K-42,K 15/3. All of them were subject to laboratory research on wall painting. Alongside of this research a great number of experimental fixation of the destroyed layer of paint was made in various monuments of culture situa-

ted in different climatic zones with severe regime of microclimate. The fixation experiment was made on less important parts of the mural in the Assumption Cathedral, such as background etc. At first the fixation was done on small areas, and as other more suitable materials were chosen these areas were enlarged. In the course of 6 years the state of the experimental layers of paint was systematically observed. On completion of the work the method of fixing the layer was submitted for consideration and approval to the experts of the comission of the State Inspection on preservation of monuments, Ministry of Culture, RSFSR. This is how the problem of accident risk paintings by Andrei Rublev and Daniel Chorny created in 1408 in the Assumption Cathedral at Vladimir was settled. The settling of the problem is also tightly connected with the study of the temperature-dampness regime in the Cathedral, and its adjustment. The constant fluctuation of this regime involves corresponding changes in the qualities of the materials of the murals and in the casein glue accumulated in the process of the frequent fixation of the layer of paint. Besides, the hyperdampness leads to the appearence of the biological agents the culture medium of which is the casein glue protein on the surface of the painting. In their turn mycelium and mold fungus have a destructive effect on painting.Therefore,

the problem of preserving the paintings may be considered as fully settled when optimum temperature-dampness indications are provided.

For two years the existing regime in the Cathedral was studied: at a definite time in different parts of the Cathedral temperature and relative dampness indications were taken and samples of stucco and masonry were studied for hygroscopic moisture. The process of the movement of moisture in the thickness of the walls and causes of breaking the regime were studied. It was found that in lower parts of the Cathedral walls at the height of 1 metre from the floor the percentage of moisture is higher in the wet season of the year owing to the sucking in of subsoil and rain water. In the middle part of the walls only the stucco ground becomes damp due to the growth of the relative dampness of the air. The reason is an irregular and at times a greater number of people during the divine service and also the absence of due ventilation and the drawing out of the air from the building. All this is aggravated by the poor system of heating. The reconstruction of the ventilation and heating systems has alleviated the situation. Now it is possible to regulate the optimum temperature-dampness regime of the monument.

A very thorough physical and chemical study of

the painting material and preservation of the original layer of paint was made and methods were found during the research work on the murals of Andrei Rublev and Daniel Chorny. It was ascertained with the help of the chemical analysis of the pigments of the paintings that the yellow, red, brown and partly green paints are oxygen ferric compounds and that in some ochre raddles a comparatively small quantity of mercurial cinnabar is introduced. Pure cinnabar was not used in the mural painting. Part of the green pigments are copper compounds. The blue pigments of the murals are all without exception natural ultramarine. Lime or chalk were used for whiting. Thus, the pigment palette of the murals was comparatively small but the colour quality was achieved by mixing the above mentioned pigments.

The chemical and petrographic analysis of the stuccoes was made, their porosity and water absorbtion were stated, which plays a significant role both in the process of restoration of the murals and in their further preservation. All the samples of the stucco prime coating are the dispersion mass of calcium carbonate comparatively equally carbonized with a small content (about5-15%) of carbonate excipient. It is characteristic that as compared with the samples of the murals of the 12th century of the same Cathedral the content of fibrillar excipient is higher. There are

grains of quartz which could have been introduced in specially small quantities or they might be a natural admixture in the limestone. The grains of the quartz are cracked. They might have been exposed to high temperature which once again proves that they are a natural ingredient of the limestone. During the petrographic analysis of several ground edges rather big fragments of brown colour were found, some of them are soft and of scaly structure typical of clay. This proves that some quantity of cement or quartz sand which might account for the presence of the clay fragments were used in the prime coating of Rublev's murals.

All the wall paintings were examined and photographed in the ordinary light rays and in filtered ultraviolet light. Numerous light spots were found on the murals of the central vault under the galleries depicting "Doomsday" They luminescein in the bright light of calcium sulphate and gyps. The calcium must have been often used for fixing the stucco ground in previous restorations. The greater number of injection holes patched with gyps were carefully covered to suit the tone of the mural. This fact not only opened a new chapter in the history of the restoration of the Rublev murals but proved why sulphate salts destructive to the layer of paint on the painting were found on its surface. Very interesting results were obtained by physical

and optical investigation of the mural on the Southern slope of the Eastern arch of the small Southern nave under the galleries. Photo fixation in ultraviolet rays showed that on the head of the Reverend Savva there are many later paintings and the original Rublev painting in this place is almost completely lost.

Since 1974 restoration work has been carried out at the Vladimir Assumption Cathedral which is a treasury of many murals, unique and valuable. Thus, about $100m^2$ of Rublev's murals, whose existence was known but whose compositions have not been photographed and published, were uncovered from under later painting of the 19-20th centuries. The most known composition "Doomsday" in the naves under the gallery is still being under restoration. The layer of paint of the murals has been fixed against accidental peeling off, and their state is being observed.

In conclusion we may say that the present day scientific restoration and a thorough study of the murals of Andrei Rublev and Daniel Chorny will help to preserve the great creations of the Russian masters for many years to come.

78/15/11

RECENT RESEARCH OF CHURCH PAINTING OF 1408 IN THE CATHEDRAL OF THE ASSUMPTION AT VLADIMIR IN ULTRA-VIOLET RAYS

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RECENT RESEARCH OF CHURCH PAINTING OF 1408 IN THE CATHEDRAL OF THE ASSUMPTION AT VLADIMIR IN ULTRA-VIOLET RAYS

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During the recent three years the restorers of Vladimir scientific restoration workshop carried out extensive preservation work and artistic decoration of the Cathedral of the Assumption at Vladimir. This has caused the necessity to fulfil a great deal of various research on murals preserved from the 12th to the 19th centuries. The investigations on physical optics have been also included in the research. The projects were realized by the specialists of the Institute "Spetsproektrestavratsija" of "Rosrestavratsija" Corporation.

The most valuable results were obtained at the observation and photofixation of murals of the 15th century. Andrei Rublev and Daniel Chorny, the greatest medieval Russian masters, were engaged on church painting. Andrei Rublev is well known abroad. In 1960 world public celebrated Rublev's anniversary on the initiative of UNESCO.

The Cathedral of the Assumption was first built in 1158 and extended by 1189. Since that time fragments of the murals have been preserved. In 1408 Andrei Rublev together with Daniel Chorny and apprentices were sent from Moscow to Vladimir to redecorate

the murals of the Cathedral.

In fact, they had to decorate the central part of the building anew. They created the most perfect masterpiece of monumental painting. The generalized outlines of the characters were brought in harmony with the ancient (12^{th}) architecture with massive pillars towering high and clear cut curves of the arches. Not only did they artistically combine the mural painting with the architecture but made it dependent on the painting. Light, almost imponderable figures and optimistic tender colouring of pure hues seemed to lift the vaults and make the massive pillars of the ancient Cathedral step apart.

Rublev's and Chorny's mural paintings were repeatedly subject to renovation and repainting for more than half a thousand years. These wonderful frescoes were rediscovered almost a hundred years ago in 1859. The purposeful restoration of the frescoes started from 1882 by the craftsmen of Safonov's workshop. The completion of the work took place only in 1918 under the scientific supervision of I.E.Grabar. During the subsequent fifty years the stucco and paint layers were repeatedly fixed, the soiling and soot being removed. But no chemical and optical research of all the murals was carried out.

The results of the first experiments were reported by V.V.Filatov at the section of restoration

in 19 and further data were published in "Reports of VCNILKR" in 19 . The results of restoration and chemical research were given in the report by L.Balygina and A.Nekrasov "Problems of Mural Preservation of 1408 by Andrei Rublev in the Cathedral of the Assumption at Vladimir."

The present report deals with the investigation in the ultra-violet rays only.

The investigation was conducted in the zone of near ultra-violet rays with maximum radiation of 365 mmk. Two silica lamps of PRK-7 type (output of 1000 watts each) actuated through throttles together with UFS-3 type filters were the source of ultra-violet radiation. Good capacity of the lamps provided intensive luminescence. After visual examination of the painting the photofixation of luminescence on the film FT-12 (sensitiveness of 90 units(21-22 din) was made. Ray filters of ZS type cutting the ultra-violet rays off and admitting the light of luminescence were set in front of the object-lens. The wide-frame camera FKD with the object-lens I-37 4,5/300 was used for the photography.

Besides, they made both the colour and luminescence photography on the colour inverse film IIT-18 with the sensitiveness of 45 units(18 din). In the first case the halogen lamp KG-220-4 with colour temperature of 3200°K was used as a source of light. In

front of the object-lens blue glass ray filters were set.

The results obtained are grouped in the following way:

- luminescence of stucco grounds and their repairs of different periods
- heightening of the contrasting tones of painting
- detection of later interference in painting

I. Luminescence of stucco grounds of different periods and their repairs.

While examining murals in UVR, various luminescence of stucco of different periods was observed. This enables us to state precisely the differences in their composition before the chemical and petrographic analysis is made. The UVR analysis of the decorations in the Cathedral of the Assumption revealed a lot of stucco holes drilled for mortar injection at the places where the stucco layer comes off from masonry of the walls and the vaults not noted graphically anywhere before. The injection holes exhibit luminescence of bright-lilac colour. Probably, they were filled at restoration in 1918 and 1931 when plaster was applied for the purpose.

On the photos the injection holes and plaster insertions looked like bright white spots. Again the lilac luminescence of the salt on the surface of the stucco layer was noted. As a rule it is the result

of the previous work on the attachment of the stucco to the masonry of the walls.

2. Heightening of the contrasting tones of painting.

The paints the chromophor of which is the compounds of ferrum-ochre, sienne of various colours and tinges do not luminesce in UVR and are taken visually as gray-black with a slight shade of brown. The dark contrast appeared not only due to the character of the pigment(yellow or red ochres) but due to the density and thickness of the paint layer and the amount of limestone whiting added to it(reduction of the degree of dark contrast). In black and white photofixation in UVR the contrasts are well fixed. This phenomenon enables us to see in UVR and to fix on wateremulsion layer the invisible and almost indistinguishable parts of the imprint. Investigating the ancient mural painting in glue-colour and distemper technique this effect makes it possible to:

- detect and fix the remains of the portrayal or the contours of the initial painting executed in ferric oxide pigments
- heighten the contrast in depicting the figures, clothes, landscape for revealing the peculiarities of brushwork and style of different painters.

Thus, in the mural painting of the Cathedral of the Assumption at Vladimir we have succeeded to reveal and fix the outline of the figures and their

elements in the places where the painting was almost completely destroyed. For example, in the group of the elders who are following the apostles Peter and Paul to the doors of the Garden of Eden.

The same contrasting effect helps us to study individual peculiarities in laying on the final strokes ("marks") onto the faces, parts of the body, hair locks as well as final white patches in depicting clothes.

3. Detection of later interference in painting.

The most unexpected thing observed during the examination of murals in the Cathedral was the later touch up of the original painting. Especially, the head of Reverend Savva on the Southern side of the Eastern arch under the Southern vaulting. On both sides of the arches like in the neighbouring ones there remained a full length depiction of the saints. On the Southern side - Reverend Savva bare-headed (kokul(headware) on the shoulders) with a broad beard split in two. On the Northern side - Reverend Antonio with thick beard in black kokul. Visually the two heads are painted in the same colour-scheme and in the same brushing. Undoubtably, the heads of both figures were authentical. Therefore the luminescence of them in UVR which differed from all the paintings of the 15^{th} century in other parts of the Cathedral came as a complete surprise.

In the face image of Reverend Antonio the marks in UVR exhibit bright yellow luminescence but in all other images they are bluish-white. On an ordinary black and white photo th "marks" look ordinary but on a black and white photo in UVR they are contrasted on the dark background of the face like ordinary limestone whiting in ochres. A more exact yellow luminescence was found not only in the lines of the marks but in the principal ochring of Reverend Savva's head image. It is noteworthy that the luminescent ochring of Reverend Savva's head image was preserved in the late limestone insertion on the top of his head. The contours of the head contrasting with black and brown tone produced by all the ferric-containing pigments are the only original fragment of brown contour in the middle right outlines of the lower part of the beard.

The examination and chemical analysis of both images resulted in the fact that Reverend Antonio's image is authentic and only the "marks" were made later not with limestone but with white lead. Reverend Savva's head image was painted anew by the scanty remnants of the original. The painting is based on white lead added into the tone of ochring. But only small parts of the original have remained, particularly - a small fragment of the outline in the lower part of the beard.

The image of the angel in the composition "The Doomsday" on the Western wall of the middle vaulting also appears to be a later masterpiece of painting.

78/15/12

THE TECHNIQUE OF CONSERVATION OF OLD RUSSIAN FRESCOES DISCOVERED IN ARCHAEOLOGICAL EXCAVATIONS

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THE TECHNIQUE OF CONSERVATION OF OLD RUSSIAN FRESCOES DISCOVERED IN ARCHAEOLOGICAL EXCAVATIONS

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The paper deals with the technique of the removal of Old Russian frescoes from the walls of the excavated buildings and their treatment for museum storage and exposition. This kind of work has been carried out on old Russian monuments since 1962. The information given in the paper is based on the examples of the restoration of frescoes from the excavated Church-on Protok (Smolensk, end of the 12th century), the Churches of St.Nicolas - of Greblya and of the Intercession (Pskov, end of the 14th century). The conservation work was carried out by the State Hermitage Monumental Painting Studio.
The routine conservation work is done in two stages - in the field and in the studio, the processes applied in both of them are interconnected. Polybutyl methacrylate of low viscosity grade (PBMA) is used as the main consolidating material. Various operations undertaken in the course of the restoration work - gluing up, surface fixation, impregnation in depth - can be carried out with the help of its solutions in different solvents or their mixtures. The reversibility of PBMA, that is, the possibility of repeated dissolution of the fixative, provides the conditions for the treatment to be continued in the studio after the fiels treatment.
The frescoes discovered in archaeological excavations are as a rule badly damaged. The mechanical strength of the plaster is usually weakened, its adhesion to the masonry of the wall is lost. The plaster layer is mostly

permeated with a net of through crackings, sometimes smached to pieces. The paint layer is often destroyed, exfoliated, and comes off the ground.

The treatment technique in tne field depends upon the conditions in which the monument is found (climate, humidity of the walls and the soil, the degree of the building's damage), as well as on the state of the building, of the plaster and the painting, of the degree of the adhesion to the wall. The aim of the field treatment of frescoes in the course of their uncovery is to retain them temporary on the wall so that the frescoes could be removed in sufficiently big fragments. The consolidation and gluing up is carried out by applying PBMA solutions. The plaster is temporary fastened to the masonry with cotton wads soaked in diluted gypsum. The uncovery and fixation is performed depending upon the state of preservation of the frescoes:

a) when the plaster is badly smashed and the bonds with the masonry are entirely lost, the uncovery is carried out in small fragments and is followed by immediate gluing with PBMA acetone solution;

b) in the case when parts with weak adhesion alternate with those of stronger bonds, the fixation of surface and the gluing up of the crackings together with the soil which fills them is also done with PBMA acetone solutions. This, in combination with the gluing up of separate parts and the applying of gypsum plugs, permits considerable areas to be uncovered and left uncovered during the time necessary for carrying out various kinds of fixation;

c) when the adhesion of the plaster with the masonry is strong, the uncovery is carried out in sufficiently big fragments. In this case, the consolidation is done by applying PBMA xylene solutions

which require much time for evaporation but provide deep imregnation.

The work to be done before the detachment of the frescoes includes markin-off, cutting the painting, gluing over, preparation of boards. The cuts to be made are marked-off so that they should go across the least important parts of the painting. The horizontal cuts are mostly marked along the dividing bands. The cutting is made with a sharp scalpel or a saw, then the edges of the cuts are thorougly glued. All the marking is fixed on a drawing with the image of all the picture on the scale of I:IO. Before the paintings are detached, they are glued over, applying PBMA acetone solution, with wide gauze bandages and two layers of gauze on top of them. According to the shape and size of the fragments to be detached sheets made of planks or plywood on wooden subframes are used. The sheet is tightly placed to the fragments to be detached, the free ends of the gauze bandage are fastened to it from all sides.

The paintings can be detached in several ways, depending upon the degree of the adhesion of the plaster with the masonry of the wall, upon the technique of the plaster layer application, upon the dimensions of fragments being detached. In all cases, the painting is detached together with the plaster layer. Detachment is followed by the fixation and gluing over of the reverse side, packing up of the painting for transportation.

The treatment in the studio consists of several stages. It begins with deep consolidation of the plaster layer by applying the PBMA xylene or alcohol-xylene solutions; here definite impregnation and drying conditions are observed. The plaster of the painting is usually permeated with a net of through crackings and practically consists of separate bits not bound with each other. That is why,

before gluing, the painting is taken apart along the crackings, the joint seams in the painting are cleaned, the deformations are set right. The gluing is carried out with PBMA acetone solution. Then the lacunae are filled with putty prepared from ground limestone mixed up in PBMA solution. The aim of the operation is to additionally consolidate the damaged plaster and to make the crackings less conspicuous. Then the surface is cleaned from dirt, the excess of the resin is removed from the surface, the texture characteristic of the fresco painting is restored (by applying some solvents or their mixtures). Much time is required to assort small fragments extracted from the soil during excavation work. The collected bits often help to fill up some losses in the picture.

The mounting of the detached paintings depends on the system of exposition. For the museum display, the paintings may be mounted in two ways - on iron sheets with wooden subframes, with the waxcolophony mixture as the adhesive; or applying polyurethane resin foamed in situ. Either method allows both plane and curved fragments to be mounted and fitted together. The mounting provides the possibility for one or several fragments to be fitted on one support, and joined together in a whole on a common construction.

Depending on the aim of the exposition, the construction can be stationary or dismountable.

The exposition is the final stage of the treatment of the detached frescoes. In museum conditions, it is advisable, to display frescoes from archaeological excavations as far as possible as a complex, arranging them according to their position in the ancient monument. Considering the fragmentary character of the murals which are usually preserved only in the low parts of the buildings, they

should not, when displayed in museum conditions, lose their monumental character, with the painting revealed to the utmost. Largely, success can be ensured by bringing the painting and the environment into proper correlation, by the colour and the texture treatment of big areas of lost painting. The display of both the frescos from Smolensk and the paintings from the Pskov Church of St.Nicolas - of Greblya was based on this principle. In the cases when frescoes are detached from the walls of the buildings which in future can be restored, it is possible to display them on the walls of the restored building, provided that müseum conditions should be created for the paintings.

The technique of mounting and fastening the frescos to the walls is a matter of individual approach, depending upon the character of the monument.

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THE EFFECT OF THE TREATMENT WITH POLYBUTYL METHACRYLATE SOLUTIONS ON PHYSICAL AND MECHANICAL PROPERTIES OF LOESS PLASTER

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THE EFFECT OF THE TREATMENT WITH POLYBUTYL METHACRYLATE SOLUTIONS ON PHYSICAL AND MECHANICAL PROPERTIES OF LOESS PLASTER

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Abstract

Characteristics of loess plaster of Middle Asian mural paintings (8th century, Pendzhikent),namely, its exposed porosity, mean diameter of pores, water vapour absorption and bending strength have been estimated. The evaluation of the changes of these characteristics after treatment with IO% polybutyl methacrylate solutions in xylene and in xylene-ethyl alcohol mixture under equal laboratory conditions has revealed no difference between the two ways of the treatment.

Some studies with a view to improve the technique of conservation of paintings on loess plaster by applying low viscosity grade polybutyl methacrylate (PBMA) is being conducted by the Monumental Painting Restoration Studio and the Chemical laboratory. As reported elsewhere (I), it was established that by applying IO% PBMA solutions in the xylene (solvent) and ethyl alcohol (diluent) mixture, it is possible under certain impregnation and drying conditions to receive deep consolidation of the painting with considerably lesser alternations of the optical properties of the paint layer than in the case of the treatment with xylene solutions of the same concentration under similar conditions. A suggestion was put forward that xylene and alcohol-xylene PBMA solutions yield a different distribution of the polymer in the paint layer

and loess plaster.
The aim of this work was to continue the comparative study of the two techniques by the evaluation of the changes of the loess plaster properties: its exposed porosity, the mean diameter of the pores, water vapour absorption (hygroscopicity) and the breaking point under static bending.
Fragments of the 8th century loess plaster, found in an excavated building of old Pendzhikent were used for the experiments. There were 3 types of plaster: reddish slightly burnt, not strong (type I), grey, more burnt, stronger (type II) and greenish-grey nonburnt, weak (type III). The plaster was probably burnt in a fire, The straw added to the plaster when it was prepared decayed or burnt down leaving here and there either big pores or charred layers. The initial characteristics of the plaster which we determined are given in Table I as mean value limits for each type (from IO-I2 tests).

Table I. The characteristics of loess plaster from ancient Pendzhikent

Tipe of plaster	Density ρ XIO^{-3} (kg/m^3)	Exposed porosity β (%)	Mean pores diameter D(μ)	Hygroscopicity W(%)	Bending strength R x IO^{-5} (N/m^2)
I slightly burnt	I,49±0,03	42,7±0,9	0,88÷I,68	I,2÷4,8	6±2
II burnt	I,48±0,04	42,5±0,8	I,36÷2,20	I,4÷5,5	29±4
III non-burnt	I,50±0,05	4I,2±2,0	I,36÷2,64	I,9÷8,6	7±2

As the plaster was not uniform, we used nondestructive methods for the determination of the mean diameter of pores, the exposed porositiy and hygroscopicity. These

methods provided the possibility of getting the characteristics for each sample before and after treatment. The samples were prepared in the form of discs with the base diameter about 3 cm and the height about I cm. The form of the samples depended upon the technique of the evaluation of the pores mean diameter which was calculated by means of the penetrability coefficient K determined under air filtration conditions approaching the laminar ones (State specification I5079-69). The exposed porosity (β) was determined according to the formula $\beta = \frac{m_I - m_o}{m_I - m_2}$, where m_o is the mass of the dried sample, m_I is the mass of the sample impregnated with the solution and weighed in the air, m_2 is the mass of the same impregnated sample weighed in the solution. Xylene was used for the impregnation of nontreated samples, water was used for the PBMA treated ones.[I]
The hygroscopicity of samples (W) was evaluated as the percentage of the dry sample mass increase resulted from keeping the sample in the atmosphere saturated with water vapours up to the constant value of the mass.
The breaking point under static bend (R) was tested on samples I,2 - I,4 cm in height, I,I - I,3 cm wide, about 3 cm long. A RS-I06 device (Hungary) was used, the distance between the supports being 2 cm. For each kind of untreated plaster I0 tests were made. I-2 samples for the evaluation of the mechanical strength could be prepared after the estimation of other characteristics from each disc treated with PBMA.
24 samples were selected for impregnation with PBMA solutions so that each type of plaster should be represented

I) In further work it was found advisable to apply in both cases n-hexane which does not dissolve PBMA.

Treatment	10% PBMA in xylene					10% PBMA in xylene-ethanol mixture				
Tipe of plaster	N° of the sample	PBMA content (%)	Porosity decrease $\frac{\beta_0-\beta}{\beta_0} \cdot 100$ (%)	Hygroscopicity decrease $\frac{W_0-W}{W_0} \cdot 100$ (%)	Bending strength $R \times 10^{-5}$ (N/m^2)	No of the sample	PBMA content (%)	Porosity decrease $\frac{\beta_0-\beta}{\beta_0} \cdot 100$ (%)	Hygroscopicity decrease $\frac{W_0-W}{W_0} \cdot 100$ (%)	Bending strength $R \times 10^{-5}$ (N/m^2)
I	I	4,3	77,6	40,0	-	Ia	3,6	71,6	32,0	-
"	2	3,9	63,2	47,0	-	2a	3,4	68,4	48,8	-
"	3	3,7	64,6	46,6	45	3a	3,6	70,0	43,0	42
"	4	3,7	76,8	46,4	66	4a	3,5	71,I	38,0	76
"	5	4,0	69,6	25,8	43	-	-	-	-	-
II	6	3,9	76,I	28,0		6a	4,2	67,0	44,7	58
"	7	2,7	54,6	33,5	60	7a	2,7	53,I	38,7	62
"	8	4,2	80,0	5I,6	73	8a	4,2	66,3	54,6	5I
"	9	3,8	71,0	43,0	75	9a	3,2	54,0	52,4	-
"	-	-	-	-	-	I0a	3,3	62,8	49,4	75
III	II	2,3	58,4	60,6	22	IIa	3,4	5I,4	62,0	35
"	I2	3,3	58,6	55,0	52	I2a	4,2	56,7	6I,I	79
"	I3	2,7	59,8	42,5	-	I3a	3,5	68,4	56,6	-

by two groups of samples with similar porosity and hygroscopicity characteristics. One group was treated with IO% xylene solution, the other - with IO% alcohol-xylene solution. PBMA with the specific viscosity of I% solution in toluene 0,32 was used. Impregnation was carried out under the same conditions of room temperature and humidity. The solutions were applied with a brush in cycles of 8-IO coatings which were repeated, as the solution soaked in, up to the saturation of the plaster. Between the cycles drying under a bell-glass during 5 days and open drying during 4 days followed. The samples were impregnated from the "face" in 2 cycles, from the reverse side in I cycle. All in all, each sample received 25-26 coatings, after which the samples were dried under bell-glasses during 5 days and not less than 3 weeks in the open air till they reached the constant mass level.

The increase of the sample mass, the decrease of the porosity and hygroscopicity indexes after treatment, as well as the bending strength of the samples treated are given in Table 2. In Table 3 the mean diameter of pores of a number of samples before and after treatment is compared.

Table 3. Mean diameter of pores of some loess plaster samples before and after treatment

Treatment IO% PBMA in xylene				IO% PBMA in xylene-ethanol mixture		
Type of plaster	N° of the sample	D (μ) before treatment	D (μ) after treatment	N° of the sample	D (μ) before treatment	D (μ) after treatment
I	3	I,00	I,I8	3a	I,00	2,28
II	8	2,20	3,88	8a	I,5I	3,00
III	I2	I,68	6,I5	I2a	2,64	5,20

The experimental data obtained speak for the fact that the plaster of the Pendzhikent paintings is not strong material with the mean diameter of the pores in the range of I,0 - 2,5 μ (in the presence of hollows up to I,5 - 2 mm). The strength of the burnt plaster turned out to be about 4 times as high as that of the nonburnt and slightly burnt plaster. In comparison with both types of burnt plaster, the nonburnt is, on the whole, characterized by higher hygroscopicity, which can be accounted for by dehydration of salts and oxides during the burning.

The accumulation of the polymer (the percentage mass content of PBMA as against the original mass of the sample) after the treatment with the PBMA solutions did not prove to be equal in different samples (from 2,7 to 4,3%). These variations are observed in cases when both the xylene and alcohol-xylene solutions are used. Apparently, they may be accounted for both by the non-uniform application of the solution in case of brush impregnation and by the peculiarities of the samples structure. On the whole, the results obtained showed no difference of any importance between the two techniques of treatment. The difference lies within the observed deviations from the average values. Thus, the porosity of nonburnt plaster in both cases decreased on the average by 59%, that of the slightly burnt and burnt plaster by 65-70%. We considered it possible to analyse jointly the results obtained for samples of the burnt plaster of both types and to establish the dependence of the degree of the exposed porosity decrease on the PBMA content. This dependence is expressed by the equation

$$y = kx \quad (I),$$

that is, the degree of the porosity decrease in the range studied is proportional to the PBMA content in

the plaster. The calculation made according to the least squares method gave for the xylene solution treatment k = I8,I9. So, according to this index, both methods are practically of equal value (see Fig.I).

The mean diameter of the pores changed after both treatments in a similar manner (see Table 3). As a rule, it increased, as the small pores became filled with the polymer and ceased contributing to this averaged characteristics.

The hygroscopicity of the plaster samples after both treatments decreased practically also equally, but to a more considerable extent in the nonburnt plaster.

The results of the bending strength tests do not permit of giving preference to anyone of these treatments either. Here there is a difference in the strengthening effect between plasters with the initial small bending strength - nonburnt (type III) and slightly burnt (type I) - and the stronger burnt plaster (type II). The bending strength of the former increased on the average by IO times, that of the latter by 3 times. Combining all the data obtained for samples of groups I and III with equal low initial strength $6 \cdot 10^5 - 7 \cdot 10^5$ N/m^2 and examining jointly all the results obtained for stronger samples of the group II, a conclusion may be drawn that the alteration of the bending strength depending on the PBMA content with-in the range studied occurs according to the equation

$$\lg y = kx + \lg y_0 \qquad (2)$$

where y_0 corresponds to the initial strength of the plaster. For the plaster of groups I and III, the dependence is $\lg y = 0{,}25x + 0{,}79$, for the plaster of group II - $\lg y = 0{,}093x + 1{,}49$ (see Fig.2). When the polymer content exceeds 4%, the bending strength of both the nonburnt and burnt plaster is about $8 \cdot 10^6$ N/m^2, though their strength before treatment was different.

Conclusion

I. 25-fold brush impregnation of loess plaster with PBMA solutions in xylene and in the xylene and ethyl alcohol mixture (I:I) under equal laboratory conditions results in similar alterations of the exposed porosity and the mean diameter of the plaster pores, its hygroscopicity and strength under static bending. The analysis of the alterations of these properties does not show any differences in the distribution of PBMA in the plaster, as the result of the two techniques of impregnation studied. Apparently, the difference exists on the microlevel.

2. In view of the nonuniformity of the samples of the loess plaster from the excavations in Pendzhikent, it is advisable in further work to use for comparative studies and quantitative evaluations of the results some model plaster prepared from loess and straw and subjected to slight burning, which would be close to the Pendzhikent plaster according to their characteristics of porosity, mean diameter of pores and mechanical strength.

Reference

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Legends to the Figures

Fig.I. Dependence of the degree of the decrease of loess plaster exposed porosity on the PBMA percentage content in it.

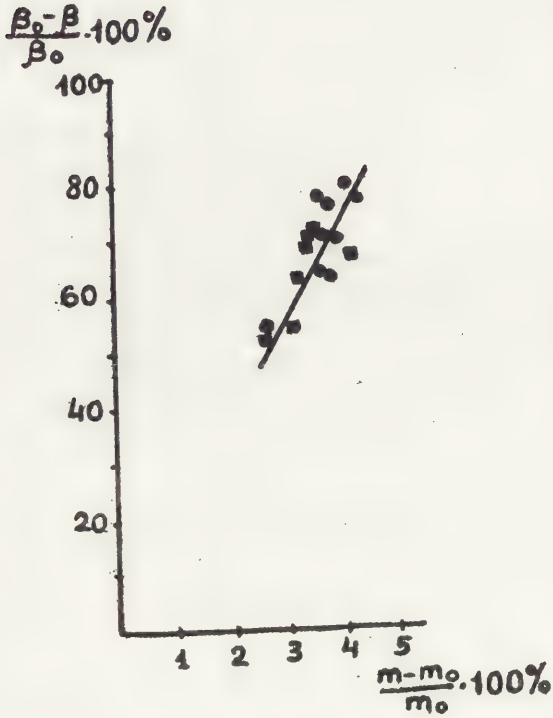
Designations: ● - treatment with PBMA solution in xylene

■ - treatment with I0% PBMA solution in the xylene and ethyl alcohol mixture (I:I).

Fig. 2. Dependence of the breaking point of the loess plaster on the PBMA percentage content in it.

Designations: ● - nonburnt and slightly burnt plasters (types I and III)

▲ - burnt plaster (type II)



$\frac{\beta_0-\beta}{\beta_0}\cdot 100\%$
100
80
60
40
20
1
2
3
4
5
$\frac{m-m_0}{m_0}\cdot 100\%$

Fig. 1

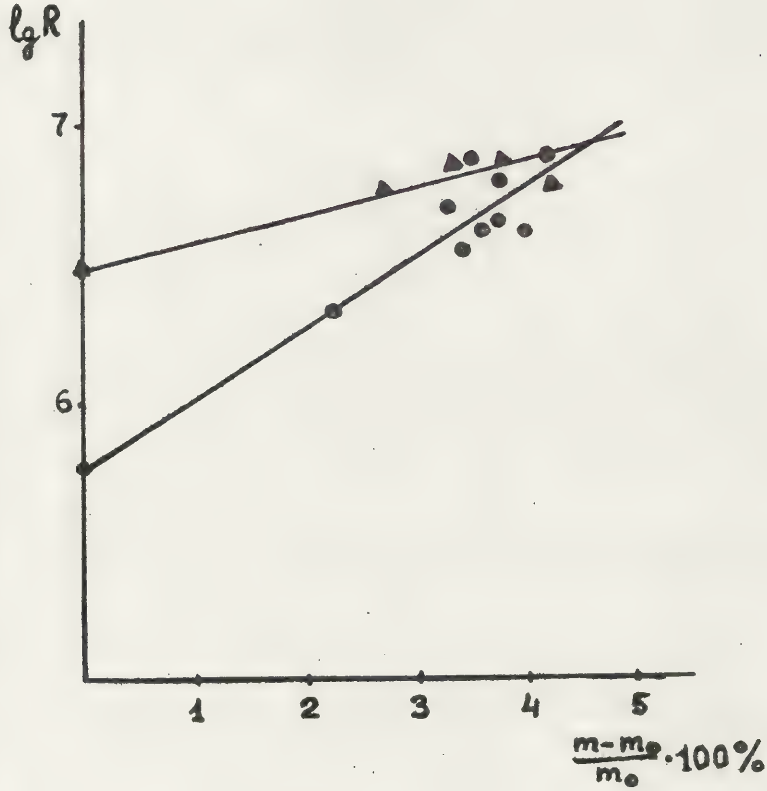


Fig.2

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RESTORATION OF ENCAUSTIC MONUMENTAL PAINTING AND MURALS WITH WAX COATING

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RESTORATION OF ENCAUSTIC MONUMENTAL PAINTING AND MURALS WITH WAX COATING

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The restoration studio receives some art monuments whose paint layer contains wax, often with different admixtures: gum, colophony and other natural resins. Such are the limestone stelae and a painting fragment from Chersonese, 4th - 3d cent. B.C., some fragments of painted plaster from a house wall from Chersonese 3d - 2nd cent. B.C., a Kerch sarcophagus, the Ist cent. A.D. Besides, it is not seldom in the restoration work that wax serves as a coating to consolidate the paint layer, as on the frescos of Raphael school in the Hermitage Museum. As is known, the encaustic painting suffers mainly from the destruction of the support, from the effects exerted by salts penetrating from the plaster thickness, from mechanical damages and mildew. The painting layer itself is stable, which is attributable to the properties of wax that forms part of the binding medium to be preserved without any visible changes during centuries. The restoration of such objects usually has the following aims: to consolidate the support, to clean the paint layer of various salt formations, of mildew stains, to eliminate mechanical damages, to fasten the paint layer to the support.

For deep consolidation of porous materials (limestone, ceramics, loess, etc.) successfully applied are polybutyl methacrylate (PBMA) solutions in various solvents (xylene, white spirit and others). As shown by routine

work, this technique may be applied to a number of objects with encaustic painting.

The restoration work is preceded by the study of the binding medium composition (microchemical analysis, thin layer chromatography and infra-red spectroscopy) and its solubility in organic solvents. Pure wax can be dissolved in different degrees in nearly all organic solvents except cold ethyl alcohol. Various compositions of the encaustic binding medium are met with, however. These binding materials sometimes tolerate the action of certain organic solvents.

The paintings on the limestone stelae excavated from the tower of Zenon, Chersonese 4th - 3d cent. B.C. and the fragment of antique portrait painting on limestone found in the same place had to be fixed before the limestone got dry to prevent the flaking of the paint layer. The painting had been carried out in the combined technique of encaustic and tempera. In this case in the field were used PBMA solutions in white spirit which ensured the consolidation of the wet material. The white spirit solvent had almost no effect on the encaustic binding material. This fixation prepared the way for further treatment of the monument - the removal of salts from the limestone.

The paint layer of the painted plaster fragments from a house wall from Chersonese, 3d - 2nd cent. B.C., also contained some wax (in a very small amount). These fragments were badly soiled with gray opaque dirt patches firmly cohered with the paint layer. In this case the property of wax to get soft when warmed was made use of in the course of cleaning. The plaster fragments were for a few seconds dipped into water heated up to 80° C. By this treatment the surface was cleaned from contamination, without affecting the paint layer. Then, after

drying. the plaster was consolidated with PBMA solution in xylene. Some tests to select both the solution concentration, which would yield optimal results for the given monument, and the impregnation and drying techniques were carried out.

In I975 a limestone sarcophagus from Kerch (Panticapaeum), Ist cent. A.D., with walls plastered and painted from the inside, was brought to the studio for restoration. The examination of the binding medium complsition by the infra-red spectroscopy method showed the presence of the wax-colophony binding medium with a considerable wax content. Some work was undertaken to select solvents which would affect the wax-resin binding medium in the least possible degree, ensuring the penetration of PBMA solutions at a required depth. It was found that the mixture of ethyl and isopropyl alcohols and xylene in volume ratio 3:3:2 give the best results. Some impregnation routine which ensured the penetration of the fixative PBMA solutions in the above solvent mixture through the paint layer at I cm depth was worked out. 5% and then I0% solution were put with a brush on the painting surface 5 - I0 times. The amount of brush coatings was regulated both by the character of the destruction of the areas being fixed and by the extent of the paint layer flaking. Uniform distribution of the polymer in the pores of the fixed material was achieved by retarded drying. The next impregnation cycle followed in 2-3 days. The number of cycles depended on the depth of the destructed area and coul be up to 8 in amount. In this way, the conservation of this antique monument was carried out.

This technique may be also applied in cases when wax serves as restoration coating which strengthens the paint layer, and its removal is undesirable. In I974-

1976 were restored two frescoes of Raphael school "Amour" and "Venus and Amour". By chemical and physical examinations the presence on the surface of wax-resin coating and gelatine glue was revealed. The latter had been used for the fixation of the paint layer. Gelatine glue with honey had been applied for the relining the fresco on canvas. The necessity to simultaneously consolidate materials with different chemical and physical properties presented certain difficulties. But the material selected - the PBMA-solution in the solvent mixture mentioned above - enabled us to carry out the restoration work: I. to consolidate the loose porous plaster; 2. to fasten it to the relining canvas in areas were their bond was broken; 3. to stick the paint layer to the support where necessary.
The peculiar character of the encaustic technique requires individual approach to each monument.

THE METHOD OF FASTENING REMOVED MONUMENTAL PAINTINGS ON WALLS WITH AIR INSULATION BETWEEN THE PAINTING AND THE MASONARY

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THE METHOD OF FASTENING REMOVED MONUMENTAL PAINTINGS ON WALLS WITH AIR INSULATION BETWEEN THE PAINTING AND THE MASONARY

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The method of exhibiting a mural removed from a wall has been substantially elaborated and applied at home and abroad. The mural is fastened on boards of various kinds of construction and exhibited in museums as easel painting. But sometimes removed murals are to be placed back on the original or reconstructed walls. If the walls are discovered in the course of archaeological excavations or reconstructed the nasonry is as a rule salt-ridden. To prevent the salt from damaging ancient murals, the latter are preferably placed so that certain space is left between the plaster of the mural and the wall.

This appears to be rather simple: the plaster with the design is to be placed on boards and put on the wall leaving some space between them, the main concern beign the choice of material for the boards. But actually the matter turns out to be much more complex.

The mural fastened on boards to be later exposed on the original wall looses its monumental characteristics and becomes easel painting, i.e., is no longer organically linked with the wall and becomes independent from the architectural monument as a whole. It cannot accentuate the plastic peculiarities of a wall made, say, of rough stone. All this becomes all the more apparent if the mural is placed next to wall paintings executed right on the masonry.

The author had to face the problem in 1968-69 when, during the excavations of the central part of

the altar of the Spas Church on Ilyin St., Novgorod, the lower belt of paintings by Theophanes the Greek (14th century) was discovered.

When the ancient floor level was reached, the ground level whithin the excavated space became 120-150 centimetres lower than the ground level outside it and the subsoil waters started damaging the unique paintings.

The plaster with the frescoes came off the wall, the painting was in a critical state. Repeated attempts by the restoration experts to fix the plaster the way it was usually done - by injecting grout - did not produce the desired results because of the dampness of the plaster and the masonry.

In 1971 the plaster with the painting was taken off the wall to be placed back later at some distance from the masonry.

The walls of this historic monument abound in painting, and the above-mentioned frescoes by Theophanes the Greek were not to disturb the general harmony. The task was made all the more difficult by the fact that it was important to take into account the line of the apse, the archaeological peculiarities of the site and the relief of the wall.

To solve this task it was necessary to make a surface that would repeat the relief of the wall in every detail and to link this surface organically with the original the way it is done when restoring easel painting. The work of this kind had not been undertaken before.

The walls of the church are made of grey limestone, dark red travertine and brick, the joints being filled with mortar mixed with coarsegrained sand.

It was evident that to follow the relief of the wall it was necessary to face the wall with elements

identical in substance to that of the masonry.

Such an element has been worked out. It is a hexagonal plate of baked clay. Its back surface is a sphere covered with glaze. There are special hollows along the sides of the plate to make cohesion with grout at the joints more reliable.

The sphere, opened from below, has six points of contact with the wall. The construction is thus stable while covering the surface of the wall to the ruinimum, and leaving enough space between the plate and the masonry.

The plates are attached to the wall with the aid of metal fastenings put into holes drilled in the wall. The plaster is fixed to the plates with grout.

The fresco by Theophanes the Greek, which is 8 sq. metres in area and presents an ornament contained in successive circles, have preserved all its monumental characteristics, and none of the peculiarities of architectural design or masonry have been overlooked.

All this makes our method much more preferable to that of exhibiting murals removed from walls as easel painting.

78/15/16

LES LIAISONS ARTISTIQUES DES PAYS ORIENTAUX CHRETIENS SUR L'EXEMPLE DE LA PEINTURE GEORGIENNE DU XIIIème SIECLE

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5ème Réunion triennale
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LES LIAISONS ARTISTIQUES DES PAYS ORIENTAUX CHRETIENS SUR L'EXEMPLE DE LA PEINTURE GEORGIENNE DU XIIIème SIECLE

Adolf Nicolaevitch Ovtchinnikov

"L'art des provinces byzantines" est un terme encore courant dans la science de nos jours: tout étonnant que cela puisse paraître, la liste de ces provinces comporte des pays où le christianisme avait été instauré des siècles avant que ne fût fondée à Constantinople la Capitale du monde bysantin. Les Etats du Sud (Est de la mer Noire et de la Méditerranée (Egypte, Palestine, Syrie, Cappadocie, Arménie, Trébizonde et Géorgie) sont liés, depuis des temps immémoriaux , par la mer, laguerre et le commerce. Malgré leur dissimilitude, ils ont eu, de tous temps, beaucoup de points communs dans leur mode de vie et leur culture. Or, à l'époque chrétienne première, cette communauté se manifestait encore plus nettement. La chrétinneté même, née dans cette région, était en quelque sorte une négation de l'Empire romain. Il en ressort que durant les 3-4 siècles suivants, Constantinople était, pour les pays cités ci-dessus, le successeur de Rome et ne pouvait être considérée par eux comme la capitale du monde chrétien.

"C'est aux provinces orientales qu'appartient le rôle décisif dans la formation du style antique avancé, il s'est développé là beaucoup plus tôt qu'à Rome à base d'une union organique des traditions de l'art antique et

Au VI-e siècle, "treize syriens" viennent en Géorgie et y posent les bases d'une culture monastique ascétique. Du VIII-e au XIII-e siècle, les peintures des monastères syriens avaient évolutionné et s'étaient développées presque simultanément avec l'art des pays de l'Orient chrétien et, en premier lieu, avec les peintures de Cappadocie. L'austère traditionnalisme de l'art oriental était également obligatoire pour les monastères de Garédji. Les rapports incessants qui existaient entre ces pays sont confirmès par l'iconographie, les procédés artistiques, voire la technologie des travaux. Ainsi, par exeple, la majorité des monuments de la peinture monumentale orientale sont exécutès sur du mortier frais avec différentes additions (charbon, sable, paille, copeaux de bois, etc.). Et c'est précisément sur un tel mortier frais que sont peintes les fresques du I-e siècle de Doura-Europos, la plupart des fresques de Cappadocie et, enfin, les fresques d'Oudabno. Les modifications qui se produisent dans l'art de Constantinople, et des écoles qui en dépendent, ne rejaillissent presque pas sur l'art monastique des cloîtres de Garédji. On admet généralement que l'art des pays orientaux se développait en tant que se développait l'art de Constantinople, mais une telle assertion nous paraît quelque peu exclusive, et il faut croire que ces pays étaient capables de se développer eux-mêmes ... . L'idée de la communauté des cultures des pays d'orient trouve sa

oriental ancien". Il en résulte que la vie culturelle de ces pays se développait de façon relativement indépendante. Dans certaines sculptures de Palmyre, aux premiers siècles de notre ère, et particulièrement dans les fresques de Doura-Europos dans le temple de Bel (I-e siècle), on voit nettement se profiler les traits artistiques auxquels Constantinople n'approchera que bien plus tard. L'archéologue anglais Briested fut le premier à éditer les fresques de Doura-Europos qu'il a très exactement dénommées "prédécesseurs orientaux de l'art byzantin". Le refus du naturalisme formel, qui caractérisait l'art romain, pouvait d'autant moins être une grossière "barbarisation" du classique. Ce refus était conditionné par les principes de l'éthique orientale, autrement dit, par des recherches d'une voie plus directe vers l'essence spirituelle de l'image. Par la suite, la Syrie, la Cappadocie, et d'autres pays, s'écarteront des modèles de Constantinople dans le même sens. La culture et l'art géorgiens se sont développés sur cette même base anti-romaine. Ce n'est ni par Rome ni par Constantinople, mais bien par la Cappadocie, en 337, que la Géorgie est convertie au christianisme. C'étaient les monastères et les ascètes, éloignés de toute activité administrative, qui étaient la véritable capitale spirituelle du christianisme.

confirmation dans l'analyse des canons iconographiques, par lesquels la mystique de l'Orient chrétien cherchait à exprimer le sens des idées essentielles de la philosophie chrétienne.

L'art géorgien dans son ensemble se distinguait, de tous temps, par son engouement pour des métériaux durs, sur lesquels les lignes sont gravées pour toujours. Et c'est, surtout dans l'architecture, la sculpture sur pierre et la repoussé sur métal, que l'art géorgien est particulièrement distinctif. De là, le caractère graphique de la peinture géorgienne, qui, au XII-e siècle, atteint à son apogée. En ce sens, l'exemple le plus édifiant nous est donné par les peintures des églises de Kintsvissi et, en premier lieu, par l'abside centrale de l'église de St. Nicolas.

Les énormes silhouettes des apôtres dans la scène de l'"Eucharistie" sont presque démunies de gesteset de mouvement. Les vastes étendues picturales des vêtements paraissent dépourvues de tout modelage et des lignes graphiques. Des surfaces colorées roses, blanches et vert-clair, lumineuses et paisibles, se succèdent sur un fond azur-clair; et donnent l'illusion de vitraux, la couleur y remplissant presque le rôle de la lumière. Cette impression se renforce encore du fait que le démembrement de certaines taches de couleur et de compositions toutes entières (particulièrement dans l'abside centrale) se conforme non pas aux registres

horizontaux mais à un mouvement vertical et libre de la luminosité colorée, qui fait chorus à la musique religieuse. Mais le caractère plat de l'application des couleurs est trompeur. En réalité, la surface de chaque tache de couleur est soumise à un modelage linéaire minutieux et infiniment complexe. Ces modelages ne forment qu'un léger contraste avec le ton dominant et n'entament pas la surface colorée, en la ravivant simplement d'un mouvement à peine perceptible; et plus le rythme général est solennel, plus cela paraît indispensable et ensorcelant. Cependant, les artistes ne se contentaient pas de modeler les formes par-dessus les taches picturales. Dans la petite église des mêmes style et époque, d'importants effritements de la couche extérieure de la peinture sur l'image, située dans la conque de l'abside de la Vierge siégeant sur un trône et tenant l'Enfant-Jésus dans ses bras, ont dévoilé toute la consécution du travail de l'artiste, qui confirme on ne peut mieux, le principe linéaire de la peinture géorgienne. Cette consécution est la suivante: par-dessus un dessin préalable, à l'endroit où devra être étaiec la couleur bleu-ciel du maphorium de la Vierge, l'artiste applique d'abord un fond de peinture gris-clair. Ensuite, sur toute la surface de l'image, y compris le fond gris, il trace en larges modelages d'étroites lignes noires, à la manière d'un négatif , sur toutes les surfaces qui devront, une fois la peinture achevée, devenir claires.

Puis, par-dessus des lignes noires qu'il laisse sécher, il applique une couche bleu d'azur profond, et procède, pour finir, à des modelages linéaires de l'ensemble, en tons plus clairs. Par ailleurs, les modelages noirs "négatifs", s'appliquent, non seulement sur les vêtements, mais encore sur les visages. Notons que la couche noire la plus prononcée correspond aux endroits des clartés maximales, ce qui explique précisément le caractère "négatif" des reproductions dans l'église de l'"Annonciation" à Oudabno (I2I2-I2I3). Il est significatif que ce procédé de modelage noir n'est utilisé que pour les images les plus importantes. Les personnages secondaires sont peints de la façon ordinaire, sur une peinture de base blanche (v. les Rois mages dans la scène de la "Nativité"). Il est à noter que cet apprêtage "négatif" des luminosités est exécuté non moins minutieusement que la graphique finale de l'éclat lumineux. Une telle méthode de peinture exige une énorme expérience, mais il apparaît que malgré toutes les difficultés que présentait cette méthode, de nombreux artistes, fidèles aux traditions de l''école de Garédji des XII-e - XIII-e siècles, l'utilisaient, plus ou moins, à cause des possibilités énormes qu'elle offrait. C'est précisément la consécution dans l'application des couleurs qui crée l'effet optique complexe, où même la couleur la plus simple commence à luire, non pas de sa couleur apparente, comme on l'observe sur une base blanche,

mais devient nacrée et mouvante, scintillante et insaisissable. A part les effets lumineux et pictureux, qu'il obtient, l'artiste est en mesure, dès le début de son travail, de manipuler les masses compositionnelles d'une manière plus précise et plus opérative. Et chaque couleur consécutive à beau être appliquée d'une manière consistante, le mouvement des modelages préalables se fera toujours sentir. La manière d'utiliser les apprêtages négatifs pour les luminosités devient connue vers le XI-e siècle dans toute la peinture chrétienne médiévale; tant à l'Orient qu'à l'Oxident. Cependant, c'est de l'Orient qu'elle a été importée en Europe. On l'observe également dans les fresques de la Vieille Ladoga, et même dans les fresques des XIV-e - XV-e siècles à Novgorod - église de St.Théodor le Stratilat, et à Pskov - église de l'Assomption à Méliotov. Mais dans tous les monuments énumérés ci-dessus, l'apprêtage négatif sous les glacis ne s'effectuait que pour les vêtements bleu-ciel et verts, et non pas en peinture noire, mais grise, parfois relativement claire. Quant à l'apprêtage noir sur toute la silhouette, voire sur les visages, il ne s'observe pour l'instant qu'en Géorgie et remonte à la peinture de Garédji des XII-e - XIII-e siècles.

Les peintures de l'église St.Georges de la fin XIII-e siècle à Atchi appartient, comme celles des trois églises mentionnées plushaut, aux traditions des centres

chrétiens de l'Orient et, en premier lieu, aux centres cappadociens, mais sont dépourvues de l'apprêtage préliminaire noir. A part leurs éléments techniques, les liens qui les unissent à la Cappadocie ressortent du choix des images de saints qui y figurent. Les dix images en buste représentent des martyrs cappadociens. L'ensemble d'Atchi est encore remarquable du fait qu'il nous permet d'établir l'époque de la coopération des artistes locaux avec les peintres venus de l'étranger. Pendant la reproduction des calques de reconstruction, on a pu très nettement déterminer la participation aux travaux de quatre peintres: deux peintres géorgiens, et deux autres, dont la manière artistique pourrait être conventionnellement nommée cappadocienne. Si nous l'appelons conventionnelle c'est parce que cette manière s'observe dans tous les centres chrétiens de l'Orient et se rencontre même dans les miniatures du Mont Athos. Les liens unissant les artistes d'Atchi à la peinture de Cappadocie et des autres pays orientaux se fait nettement sentir dans les motifs ornementaux spécifiques que l'art byzantin classique ignorait. C'est, tout d'abord, le feuillage ornemental d'un dessin spécifique.

La diversité de la peinture de ces deux groupes artistiques est évidente. Le caractère ethnique est très nettement rendu dans la peinture des visages. La comparaison entre les procédés artistiques des peintres locaux et des artistes étrangers exige une analyse plus

minutieuse. Nous nous arrêterons, pour ce faire, sur les compositions représentant la Présentation de Jésus au Temple et l'Ascension. La méthode de l'aîné des deux peintres cappadociens consiste en un minutieux travail préliminaire, autrement dit, en une corrélation exacte de la composition avec l'ensemble général, à chaque étape de son travail. Le peintre étudie longuement et attentivement l'harmonie picturale, en s'écartant plus d'une fois assez considérablement du dessin premier. Cependant, l'objet de sa préoccupation ne consiste pas uniquement en ladisposition formelle des masses compositionnelles. La posture et l'expression de chaque personnage sont subordonnées à l'intonation même de la scène reproduite, et cette intonation détermine le caractère du rythme pictural et linéaire dans tous les éléments de la composition. Cette intonation déterminée est, en quelque sorte, codée dans chaque processus du travail. Le calcul de toutes les étapes préliminaires permet au peintre de réduire au minimum l'application des glacis. Le premier des peintres géorgiens, l'auteur de l'Ascension, divise les étapes de son travail dans l'ordre suivant: un dessin préliminaire est fait en ocre claire et suivi d'une couche de couleurs assez simple; presqu'applicative. Les glacis sont beaucoup plus nombreux dans sa peinture que dans celle de ses confrères cappadociens, mais ils assument alors presque toutes les

fonctions plastiques. Ce sont eux, uniquement, qui éclairent et déterminent le sens de chaque image, ordonnent rigoureusement les taches picturales, font ressortir tous les accents rythmiques de la composition, autrement dit, nous dévoilent l'essence même de l'idée compositionnelle. Contrairement aux artistes cappadociens, le glacis de l'artiste local n'unique pas la direction que doivent suivre les lignes, mais accompagne le mouvement de chaque ligne et de chaque forme jusqu'au bout. Et, d'une façon général, la constance et l'indépendance de la culture artistique des pays orientaux vis à vis de la culture byzantine avaient été relativement de longue durée, particulièrement dans les milieux monastiques. Les peintures des monastères de Garédji, qui doivent leur origine au monachisme syrien, en sont une preuve de plus. S'appuyant sur une pratique ancienne, ils ont donné naissance à de nouvelles traditions, puisées dans l'expérience spirituelle de leur peuple.

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STUCCO AND ITS POLYCHROMY: HISTORICAL AND TECHNICAL SOURCES AND PRINCIPLES OF EXAMINATION AND RESTORATION

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Abstract

Stucco-ornaments form an integrate part of wall-decoration indoors and outside from antique times up to 1900. They are very often painted or coloured in different manners and techniques. The principles of which and their geographic and chronological developments and modifications are only little studied till now. Historical, technological and scientific examination of stucco-work and colours used is requesting, giving some examples. Finally more respect, precisation and carefulness is demanded. The same ethics should guide the restoration avoiding a total renovation of colours or metal-applications as unfortunately often can be viewed.

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Stucco techniques

Stucco means work of anorganic materials which can be modelled by hand or wooden tools for creating reliefed or full-size figures or wall bound decorations. There cannot be given any definite recipe of content, which depends on local sources and traditions of this profession in history. Lime and/or gypsum powder with or without organic mediums and glues are possible and have been

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used together with a wide range of sand, common ones or marble powder etc. (1). Already in the 16th century "Gips-arbeit" was used as german synonym to the italian term of "stucco" (2). But only from the late 18th century upwards the term "stucco" concentrated to the exclusiv meaning of gypsum-work like the tradition of this handicraft did (3). In this late time casting and printing of stucco -decorations was preferred too, as it had been in the 16th and early 17th century and perhaps in ancient Rome. But as for Austria f.e. all stucco-work of north-italian or native craftsmen[3a] between 165o and 175o has been modelled freehand. The black charcoal or red underdrawing with construction lines onto the plain wall is often to be seen where the plastic stucco is lost. It must have been necessary- and can be proved when reconstruction-work is done today (4)- to execute greater composions like a ceiling or else by adding "giornate"similar to frescoe-techniques, yet we are hardly able to find them after drying, lime-priming, colour-layers and later cracking. The very quick execution of stucco-figures by Italian specialists in the 17th century we konw of by several notes f.e. about the work of the Carlone brothers 1682 at the monastery at Garsten, Upper Austria: nearly every day a small angel and every second day a life-size one were finished. (5). The frequent construction principles of wooden ceilings with reed mats, water preserving charcoal-fillings for greater bodies etc. have been studied in detail at the Dientzenhofer-building of the New Residence at Bamberg (6). This may be one of the basic differences to ancient times and the early traditions of Renaissance when stucco primarily was put to brick walls or constructions of tufaceous stone like often in grotto-decorations. Consequently the competent writer of Renaissance like Vasari in the foreword of his "Vitae" (155o, sculpture, chapt.VI) followed closely the descriptions of the antique forerunners (Vitruv, book 7, chapt. II,III,VI ,Plinius book 36)

Unfortunately the methods of scientific analyses of the hydraulic components and the different modifications of lime (slaked lime and marblepowder fillings) offer some complications that so far no reliable data are published on our subject.

The historical evidence of some recipes given in the literature as 2/3 lime, 1/3 marblepowder (Vasari) or travertine (Sansovino 6a) or 2 parts lime, 1 part sand, 1 part gypsum for stucco in Germany about 159o (7) will first have to be examined and compared to other results obtained. Even more dubious are indications that medieval stucco-works only consists of gypsum (8).

Methods of Polychromy

The basic appearance of stucco is that of no colour, that is the pure white of its material consisting of like the descriptions by Vitruv, Vasari or Sansovino confirm. The relevant decorations are composed of stucco-pastes made in their uppermost layer thoroughly of lime-bound marble-powder very similar to the still vivid plaster-tradition of "marmorino", a technique used at the famous buildings of Palladio and common in Italy till nowadays. (9) On the other hand the majority of white baroque stucco besides this special "marmorino"-tradition seems to have been slightly whitewashed with lime-milk in wet or/and dry state. The artistic value of this operation became evident at the actual restoration of the vaste painted and stuccoed vault fo the monastery Stams in Tyrol. The stucco-decorations had been performed in 1731 by bavarian craftsmen (Franz Xaver Feuchtmayr and Josef Fischer) and not undergone substantial later alteration: the pretty arrangements of flowers fruits and leaves are still left in their natural egg-white surface of the fresh modelled stucco whereas all bodies of angels or puttos are softened by a white brushing , the margin of which rested visible at the back of these figures.

For coloured stucco-decorations, ornamental and figurativ ones, two great groups are to distinguish from ancient time onwards:

1. surface painting, gilding or other application of metals,and
2.colouring of the upside stucco layer by adding pigments.
The latter way of mixing the colours just to the wet material can often be found in connection with mosaic-techniques from ancient up to medieval times to avoid the bright disturbing effect of the filling plaster inbetween the single mosaic-stones (1o). Furthermore we find similar methods with Roman wall-paintings or terrazzo-incustations, although these mainly reddish-coloured layers (brickpowder) have a more technical function(retentation of water-content)than artistic value.

Questions of invention and execution

Above all the second technique proofs the responsibility of the stuccoer himself for the execution of colouring. Moreover we know by written sources that painting of stucco has been due to the stuccoers profession as many documents call upon this fact (11). Normally the patron had to take care for sand, lime and gypsum, but the colours used were put into account by the stuccoer (12). Further we have to keep in mind the special but not seldom cases, when artists had been active as painters and stuccoers too as some Italiens and later on German artists did. For example in Austria Giovanni Battista Barberino in the 17th century or in Bavaria the Asam-and the Zimmermann-brothers in the 18th century (13). Only the gildings were normally executed by special craftsmen, as the "kurfürstliche Hofvergolder Georg Frühholz" from Munich did in 1746 for the Upper-Austrian Monastery-church in Wilhering near Linz (14).

In central-european baroque of the 18th century genious architects like Johann Lukas Hildebrandt or Balthasar Neumann have to be viewed responsible for the colour compositions of stucco in their buildings. Hildbrandt,educated during the late 17th century in Rome at Carlo Fontana, promised in 1722 to come to Linz to look if the stucco colours in his newly built Deutschordenschurch would be agreeable to his taste and designed himself the colour pattern of the gallery-parapet.

The painter Martino Altomonte wanted in connection with Hildebrandt to explicate the colours to the stuccoer and be present at the necessary proof (15)Sometimes the function of the painter became predominant like at the castle-chapel of Meersburg 1741, where the stuccoer Joseph Anton Feichtmayr was forced by the patron to take orders from the painter of the ceiling Gottfried Bernhard Götz, and in the presbytery of the basilica at Einsiedeln in Switzerland, where the painter Franz Xaver Kraus had to compose the stucco colours in 1746/5o (16). Returning to Balthasar Neumann contracts fo this architect with the executing stuccoer are known (church of Limbach 1753) determining literary the colours of stucco and wall. Moreover with the name of this architect is connected a most interesting collection of coloured stucco-designs (the socalled scetchbook of Balthasar Neumann), which is conserved at Würzburg (17).

The questions of colour-material and colour-style

Likewise the stucco-material itself is a lack of scientific examination of the colour-materials too. Yet by means of historicalsources we know something about. On colouring of the gypsum with glue- or gum-water similar to the marble imitation on gypsum-base (writes Cröker 1729 in his handbook giving some recipes for mixtures: Orpiment and Indigo for green, a sort of Florentine-Lacque with gypsum and soot for pinkred, Indigo for blue, cinnabar or brazilwood with gypsum for red, Orpiment with cinnabar and soot for yellow (18). These indications may be proved and amplified by individual notes like bills on special colour materials etc. Thus we are told about pine - soot, Indigo and glue 1648 for Seitenstetten, Lower-Austria, (19), Englishred, Hungarian Malachite, yellow earth and pine-soot 1722 in Linz (2o) , azurite and malachite, cinnabar and minium, kettle brown, silver-litharge and lead-white 1757/58 in the cathedral of St. Gallen in Switzerland. There microscopically only azurite and malachite had been examined during the 1967 finished restoration whereas no lead-

whitewas proofed and the red and yellow original tones assumed to be earth-colours (21). Stucco gildings of the early 18th century nearly always consist of true burnished gilding or silvering on the base of chalk-glue-priming and bole-layers. But only few places of good climate show well preserved baroque stucco-gildings, in consequence to high humidity of walls and air like the great baroque church of Melk, Lower-Austria(still to-day more than 8o% r.h.), where the burnished wine-spirit-gilding of 1723 ff. had to be renewed in 1773 by means of the less weak but mat oil-gilding. Remarkable are different metal applications according to the taste of the time: bronze or copper leaves, red, whitish- or citron toned goldleaves, that can be found from about 16oo onwards. Copper-alloys are often seen to have altered into a darkbrown irreversible state. This could be examined at the Palais Attems in Graz (ca. 17oo) and may also be the fact with the stucco decoration ot the Trinity church of Novate Mezzola (1715), where no gold could be foundbut only copper and zinc, that by discussion was given to a later restoration without keeping in mind the different metal-application-techniques of baroque stucco. (22) Finally we may not forget the numerous application-materials that had been used in connection with stucco-and plaster decorations: black, white or coloured stoen grains, glass-powder, eggshells or conchs, small mirrors etc. that could be pointed out by painted shadow-strips too as we find in the fantastic grotto-decorations of italian tradition of the 17th century (f.e. Villa d Este in Tivoli, Gabriel-chapel in Salzburg, Munich-residence grotto court, Sala terena at the Traun-castle in Petronell, Lower-Austria).

Coming to stylistic developments we can view a more or less international unity depending on the characteristic export of stuccoers from the southern region of the Alps all over Europe (23). These regions in Lombardia, (the Valli Intelvi) in Graubünden (Misox), in Bavaria (Wessobrunn), in Vor-

arlberg (Bregenzerwald), and some others dominated with their travelling specialists many countries in the 17th and 18th century , after the first italian craftsmen had brought the new use of stucco to Germany around 154o. Therefore none or only little personal or national styles are important, but characteristic combinations of different techniques of painting and colouring according to time and building-category (sacred, profane, grottos etc.). Knöpfli has tried to give a brief summary of possibilities, yet we confine to a mere record in the chronological sense, that in reality has richly been combined, playing with colours within the stylistic principles of the single periods.

a) uncoloured, white, grey: from 16th to 19th century. combina tions with white walls, with parts of thoroughly coloured pink or green leaves or figures (f.e. Carlone in Garsten 1684, Schmutzer in Wessobrunn 168o ff), white egg-moulding-patterns with blackish underlayer for deep"shadows" (f.e. Salzburg cathedral ca. 163o see Fig. 1 and 2).
b) white stucco to coloured wall-plains: 16th to 19th century. Blue, green or red segments or squares painted or thoroughly coloured inbetween the different ornament styles of stucco (from the arabesque to akanthus and style Berain to Neo-Classic): f.e. Passau, cathedral ca. 168o or castle Pommersfelden, porcellain-cabinet 1718).
c) stucco intensively coloured: 16th to 18th century. Combinations with white walls and coloured stucco-paste (1o different colours: Salzburg, Neugebäude ca. 161o (24), with rich finted marble imitation to the walls and gildings etc. (f.e.bishop-residence at Kempten, ca. 172o)
d) guilding or other metal-application, lustre painting (on gold or silver): from the 16th to the 18th century combinations of pure gilding to white walls (f.e. Venice, Palazzo ducale, 16th century, castle Vaux le Vicomte, 1661, Vienna, Schönbrunn-castle, ca. 177o), gilding and silvering

with lustre painting (Freiburg/saxonia, cathedral, presbytery 1594,[25] Graz Palais Attems, ca. 17oo, Würzburg, residence, mirror-cabinet, ca. 175o), gilding and silvering to coloured walls (f.e. Munich, Amalienburg, 1734 ff.)

The principles of changing colours within a given scheme shows the "Balthasar Neumann scetchbook" cited above, where some ceiling-drawings are divided into 3 or 4 different colour-compositons.

Examination and Restoration

Finally we must call upon the stratigraphic method of examination of the sometimes thickly overbrushed stucco-works by every cautious and sensitive mechanical scratching. Wet methods or air-abraisisives must fail due to the weak surface-structure of a lime- or glue-bound stucco-polychromy. One of the most frequent and severe mistakes in stucco cleaning consists of scratching too deep, neglecting the original surface of stucco. Normally the latter is strangly indicated by a dark layer of patina which can help to define clearly the level to stop. This patina sometimes adheres so intensively to the polychromy that no further cleaning of colours would be possible than destroying them. Inthat case the polychromy should better be renewed on top of the darkened original. The binding mediums used for the new polychromy should be chosen after the original ones: glue-or limebound, opaque or glazing aspect of the colours laid on. Whenever possible the original aspect of the stucco-polychromy should be conserved and only the patinas reduced by using soft or harder erasing gums. When some alterations of colours or metals are to be found irreversible they should be preserved to the rule of respecting the true original better than renewing in a doubious way in

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a different modern manner (as f.e. Yugoslavian restorers did at least at the Palais Attems in Graz, which after restoration of copper applications etc. looks like a new-rich disgusting modern appartment). The rules of the 1964 international Venice-Charta are valid in this field too.
For documentation seldom the ideal base of complete diagrams of stucco-composition f.e. by means of photogrammetric plans is available. But as in the field of polychromed sculptures or colours in architecture records of the different super-posing colour-compositions coming from origin to later alter-ations should be given. A very solid and practical system of examination-sheets recently has been developed at the work-shops of the Bavarian Monuments Service in Munich, that is just in use with the actual restorations of interior deco-rations of this country. On examination-methods, analyses and restoration-problems of polychromed stucco in Switzerland speaks Knoepfli in a recent publication (26). There also the very important question of distinguishing grey or blackish patinas from similar colouring is discussed.
At least if possible at just missing parts of stucco-deco-rations small pieces of original stucco-substance with the relative colours can be taken during restorations for storing in special material-collections of which f.e. the workshops of the Bundesdenkmalamt in Vienna own some 5o pieces from stucco-works in Austria from the Roman period to the 19th cen-tury.

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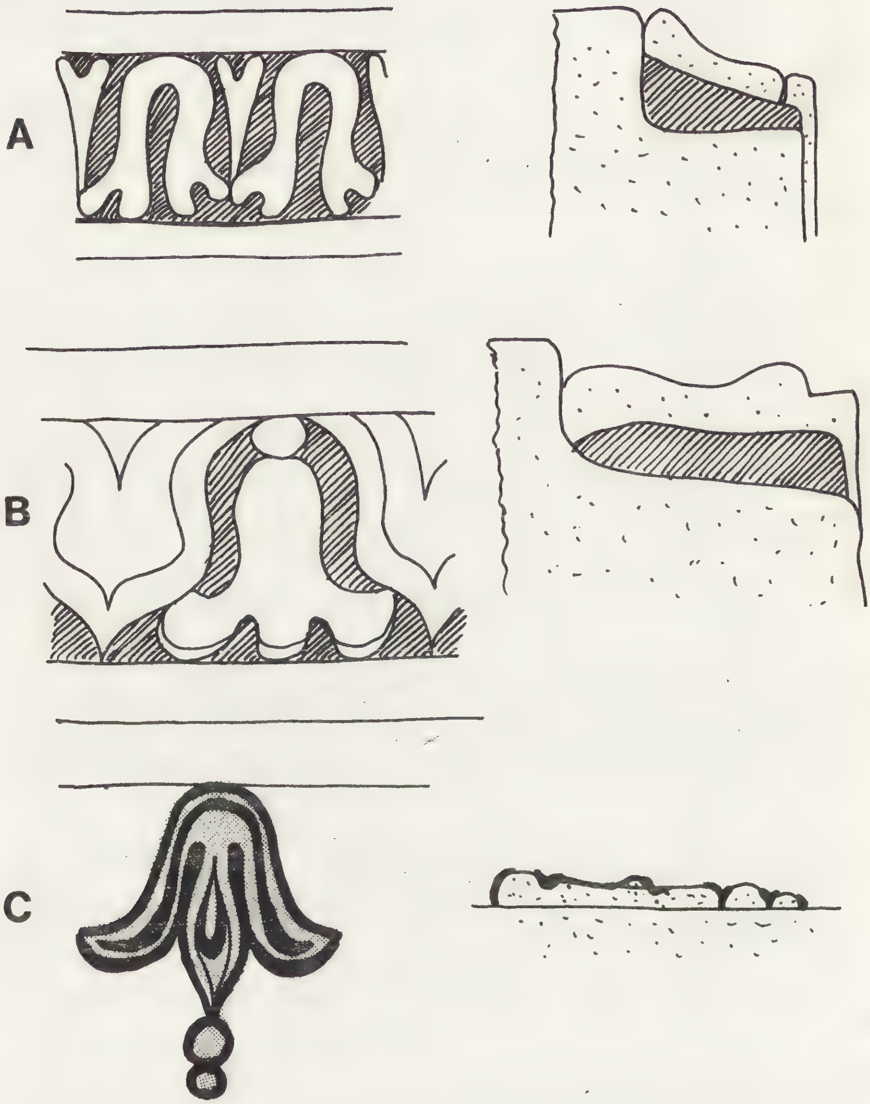

Fig. 1 : Methods of stucco-polychromy in 17th century

A) Kremsmünster, old sagresty (white/blackish)

B) Salzburg, cathedral, ca.1630 (white/blackish)

C) Scharnstein,OÖ., castle (red and darkred painted on white)

78/15/18

LES FRESQUES DU TRECENTO DANS LA CHAPELLE SAINT-ETIENNE A ZAGREB, LEUR EXECUTION TECHNIQUE ET LA MANIERE DE LES PRESENTER

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LES FRESQUES DU TRECENTO DANS LA CHAPELLE SAINT-ETIENNE A ZAGREB, LEUR EXECUTION TECHNIQUE ET LA MANIERE DE LES PRESENTER

Ana Deanovič

Résumé

Les peintures murales découvertes dans la chapelle de l'archevêque Etienne à Zagreb seraient de la deuxième moitié du XIVe s. La technique de l'exécution, l'iconographie et le style les rapprochent de la dernière phase de l'activité des ateliers des maîtres de Rimini. La technique en fresco-secco suit généralement les conseils du Traité de Cennino Cennini, ainsi que certaines idées du prêtre Théophile. La palette en général est composée de couleurs minérales sauf le bleu qui est obtenu par le smalt, et les noirs organiques. Toutes les connaissances sur le métier du maître ont donné un indice précieux dans le domaine de la conservation de la peinture murale, ont apporté aussi à la présentation même, partant en premier lieu du caractère décoratif de la peinture murale. Les fresques présentant par la force de leurs coloris, de leurs qualités historiques et esthétiques, le décor prédominant de l'espace de la chapelle, formaient aussi le point de départ de l'harmonisation de tous ses divergents et différents éléments.

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Dissimulée par les bâtiments de l'archevêché de Zagreb, la chapelle de l'archevêque Étienne a conservé dans ses murs de diverses époques de nombreux souvenirs de son lointain passé. Les murs lisses de son petit espace qui n'était éclairé que par deux fenêtres néogothiques ont permis de faire lors des travaux des trouvailles préromanes passant surtout du gothique au baroque, présentant des métamorphoses de ses premières apparences.

L'initiative première pour l'entreprise de ces travaux a été la trouvaille fortuite des peintures murales. A l'issue de l'intervention du Service des monuments historiques de la R.S. de Croatie de 1949 à 1953, il ne fallait plus songer à rendre à l'intérieur de la chapelle son aspect baroque, les fresques du trecento sauvegardées en partie sur les voûtes et sur les parois donnant une autre image qui exigeait la

valorisation d'autres éléments gothiques de l'espace, tel que l'abaissement du plancher à sa hauteur première. Outre la dimension de l'espace qui grâce à cela a pris des rapports plus authentiques en ce qui concerne les fresques, les fenêtres gothiques alors dégagées ajoutaient à cette ambiance gothique par la lumières qu'elles apportaient. Pour réaliser cette diffusion de la lumière dans la chapelle, il a fallu procéder à l'établissement d'une liaison entre les fenêtres gothiques de l'intérieur et celles de style baroque de la façade au moyen d'un conduit spécialement pratiqué pour amener le maximum de lumière.

Pour conserver les fenêtres gothiques du mur principal il a fallu enlever le retable baroque. Sur les empreintes de l'ancien autel dans les fresques, un nouvel autel a été reconstruit. A la place du retable, un crucifix gothique en bois provenant de la cathédrale y a été transporté également dans le but de redonner l'idée de la fresque représentant une scène du Golgotha. Cette fresque ayant été presque entièrement détruite par le percement de nombreuses fenêtres et par la pose du retable de marbre. Cela a donc été l'unique façon d'évoquer le sujet de la fresque disparue et de retrouver les fragments épars, le rapport existant avec le sujet central, le Christ en croix, bien qu'apparaissant ici sous forme de sculpture.

Les détails architecturaux dont l'apparition a provoqué la destruction des parties anciennes ont été maintenus sur les parois de façon plus ou moins accentuée suivant leur valeur historique et leurs qualités esthétiques et ainsi mis en harmonie avec le reste des fragments des fresques par la couleur et par la forme partout où les espaces vides des peintures murales le permettaient.

Les fresques présentant par la force de leurs coloris, de leurs qualités esthétiques et historiques le décor prédominant de l'espace, formaient le point de départ dans l'harmonisation de divergents et différents éléments. Il s'agit en effet de la deuxième couche des fresques de la deuxième moitié du XIVe siècle, cette couche recouvrant autrefois toutes les voûtes de la chapelle, son côté sud, est et en partie son côté ouest où le travail entrepris avait été subitement interrompu. Non seulement les fresques étaient inachevée, mais elles étaient aussi très endommagées par les intempéries et par les transformations ultérieures. Bien que dans cet état, elles offrent suffisamment de données pour une reconstruction iconographique et un programme décoratif et nous révèlent l'appartenance à un style et à l'expérience technique d'un maître italien inconnu. Les fresques découvertes représentent par leurs qualités et par leur particularité de style, l'oeuvre qui par sa signification dépasse le cadre du pays. La technique de l'exécution de l'iconographie et le style même de la conception les rapprochent du cercle de l'école de Rimini de la peinture du trecento, mais ces

fresques ont malheureusement été détruites par les deux dernières guerres ce qui en a réduit encore davantage le nombre. Les fresques, d'après leurs traits marquants appartiennent à la dernière phase de l'activité des ateliers des maîtres de Rimini au moment de la dispersion et de leur entrelacement avec les écoles des trois Venises déjà très affirmées. De ce point de vue, la découverte de la peinture murale dans la chapelle de Zagreb contribue à l'étude de la peinture du trecento ainsi qu'à l'orientation du développement et de la technique de sa peinture murale. Aussi, non seulement une valorisation historique et esthétique de l'oeuvre s'impose, mais également une présentation attentive de la technique de cette peinture.

La technique de la fresque suit généralement les conseils du traité de Cennino Cennini ainsi que certaines idées du prêtre Théophile. Sur la première couche de peinture murale, le peintre répartit par larges touches de couleur rouge (sinople) les registres déterminés dans l'espace destiné à " la journée". Sur ce fond qui n'a pas été gratté au préalable on passe un crépi pour la fresque d'une largeur de travée d'environ 5 m et d'une hauteur de 60 cm.

Les travaux de la fresque commencés par la partie supérieure en allant vers le bas, mais la partie inférieure est restée inachevée hormis la paroi principale. La surface crépie (crépi auquel a été ajouté du sable fin de calcaire) soigneusement polie sur laquelle sont posées des auréoles en relief de plâtre gravé de cannelures et du contour des têtes des saints.

Le fond bleu a été peint tout en ménageant des espaces vides pour les figures devant y être réalisées. Les parties nues du corps sont peintes avec une technique "ad impasto" dans les tons rouges soigneusement nuancés sur fond jaune ocre comme le faisait de temps à autre Giotto, contrairement au ton vert ("verdaccio") employé jusqu'alors. Les lumières ("lumeggiature") sur les visages et les membres ont été rendues d'après Théophile, alors que les cheveux et les barbes l'ont été d'après Cennino Cennini, ainsi que les draperies partant du ton le plus foncé vers le plus clair par le mélange graduel du blanc. Les ombres sont rendues le plus souvent par une autre qualité de couleur (en posant du noir ou du bleu sur du blanc, du rouge sur du jaune, du vert sur le rouge et inversement).

Bien que les coloris donnent l'impression d'être très riches, une palette très simple a été utilisée (en général composée de couleurs minérales).

Les valeurs achromatiques se succèdent allant des blancs (kaolin) aux noirs (d'origine organique).

Les impressions les plus fortes sont suscitées par les bleus prenant toute leur valeur en premier lieu sur le fond. Ces bleus sont obtenus par le smalt, pigment vitreux révélé également dans les fresques de Constantinople datant de 1325 de la mosquée Kahriё par Rutherford Gettens, Stout. Ce smalt a pour support le noir organique ou la terre verte. Quant à la couleur verte elle prend toute son intensité par de jolis tons de terre verte allant du bleu de glauconite au céladonite; mais les couleurs rouges dominent sur une vaste échelle allant du rouge au violet. (les rouges obtenus par l´argile et les violets par l´hématite avec du noir). Les jaunes ocres dans ces nombreuses nuances sont de composition minérale différente. La composante de fer se présente sous forme de limonite ou goethite. En ce qui concerne le rouge, il n´y a que le cinabre qui pourrait être artificiel et qui est toujours posé sur un fond d´ocre rouge.

Technique: "fresco-secco". Les couleurs sont toujours pures excepté le mélange avec le blanc et le noir. La caseine sert de liant. La couche de peinture est la plus épaisse sur les endroits des "lumeggiature". En plusieurs endroits on constate deux ou trois couches de couleurs superposées. Sur les vêtements du Christ et ceux des anges en plusieurs endroits, dans l´esprit du costume italien du trecento on a constaté par les ultra violets filtrés les restes de la colle dont on s´est servi pour l´application des feuilles d´or. Pour obtenir toutes ces données, nous avons procédé aux analyses microchimiques et microscopiques des échantillons, à la diffraction des rayons X, aux recherches minéralogiques et pétrographiques et à la photographie par la lumière monochrome (UV, IR).

Toutes ces connaissances sur le métier du maître ont donné un indice précieux dans le domaine de la conservation de la peinture murale. Ces données ont apporté une aide précieuse lors de la présentation même basée en premier lieu sur le caractère décoratif de la peinture murale, ce qui signifie que dans la restauration des peintures, nous avons avant tout souligné la répartition des parois d´après des registres déterminés sans prendre en considération la quantité des vestiges des fresques: ont été restaurées toutes les bandes décoratives qui séparaient les registres et les compositions et a été rétabli le fond bleu là où cela a été possible. La succession des figures dans des champs séparés se réalisant dans un rythme déterminé et avec symétrie reprend vie par le fond bleu autour des figures: les parties claires sont cernées par un contour et là où la figure se devine à peine les lignes sont estompées suivant la conception du travail du maître. Pour conserver le plus possible le caractère authentique de l´oeuvre on a introduit des détails de restauration dans deux figures parallèles plutôt sur l´une que sur l´autre. Moins la figure

est endommagée et plus le ton local restauré est proche du ton original. Par contre, plus la figure est abîmée, et plus la couleur locale restaurée est pâle, si bien que la figure intégrale semble estompée.

Ainsi, a-t-on essayé de conserver la matière du monument gravement endommagé, d'évoquer l'hétérogénéité de son passé en prenant garde à ce que le tout forme une harmonie esthétique qui par les rapports harmonieux de ces nombreux détails esthétiques et historiques retiendra l'attention du visiteur. Quant à la restauration même, elle a contribué à faire naître en nous le sentiment du beau et à en faire connaître l'historicité.

PROTECTIVE COATINGS, TRADITIONAL AND MODERN

Coordinator : R.L. Feller (U.S.A.)
Assistant coordinator: E. de Witte (Belgium)
Members : J. Ainaud de Lasarte (Spain)
N. Baer (U.S.A.)
P. Cadorin (Switzerland)
M. Kirby Talley (Netherlands)
A. Ivanova (USSR)
F. Mairinger (Austria)
G. Mâle (France)
P. Mora (Italy)
I. Nazarova (USSR)
J. Plesters (U.K.)

Programme 1975-1978

1. Historic references to varnishes (Plesters, Mâle, Ainaud de Lasarte, Kirby Talley).
2. Modern synthetic resins (Feller, Baer, De Witte, Mairinger, Cadorin).
3. Application of varnishes (De Witte, Feller, Mora).

AN EXAMINATION OF VARNISH FROM THREE EIGHTEENTH CENTURY MUSICAL INSTRUMENTS

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AN EXAMINATION OF VARNISH FROM THREE EIGHTEENTH CENTURY MUSICAL INSTRUMENTS

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ABSTRACT

Varnish samples from three 18th. Century stringed instruments were examined by gas chromatography. No evidence was found for the use of glue or egg-tempera as a priming. In each case, pine resin and walnut oil were found. Varnish from a Tononi cello appeared to contain some mastic and beeswax.

Of late, there has been renewed speculation on the composition of the varnishes employed by the Old Master violin makers and the acoustical influence that certain types of varnish base would confer on such instruments. Recently, this laboratory carried out chemical tests on the varnish layer of three 18th. Century stringed instruments. The samples consisted of fragments of wood, complete with varnish. In each case, it was understood that apart from the possibility of some residual shellac polish - French Polish, the varnish was considered to be as applied by the maker of the instrument. The details of the three specimens were as follows:-

1).. The top of a Serafin violin. Venice, early part of 18th. Century.
Sample dimensions: 1 cm. x 1 cm.
A pale, clear varnish.

2).. A Zanetto viola top. Brescian, probably early 18th. Century.
Sample dimensions: 1 cm. x 0.8 cm.
Slightly darker than above and clear.

3).. Rib from a Tononi cello. Bologna, early part of the 18th. Century.
Sample dimensions: 2 cm. x 1 cm.
This varnish was of a very dark, red-brown colour and had a slightly matt appearance.

Throughout this study, it should be emphasised that the analyses have been carried out on the complete varnish layer; it was not possible to have sections prepared. Portions of the varnish were taken by means of a scalpel blade and a low power hand-lens, but only after degreasing the surface by swabs, moistened with benzene. This was to ensure the removal of finger grease and wax polish.
Of the three samples, all were found to contain ninhydrin-positive material, but the intensity of reaction was little more than that of the blank controls. Furfural tests were carried out on the samples. Each gave a weakly positive result. This probably represented little more than traces of woody fibre, accidentally removed when scraping the varnish. These results indicated that in these three instances at least, no significant amount of proteinaceous material, such as

glue or egg-tempera, had been applied as a priming to the wood.

The ether/methanol solubles of the varnish from the Serafin violin top were subjected to analysis by gas chromatography, before and after methylation. The chromatograms exhibited several features of interest and, for the most part, suggested a varnish based on a conifer resin. All of the main peaks resulted from acids. The main volatile component was identified by its retention characteristics as dehydroabietic ester. As has already been mentioned in a previous publication (1), during the ageing process, abietadiene acids gradually rearrange and lose hydrogen to form this acid. Further oxidation of this component takes place to form 7-oxodehydroabietic acid. This compound, as its ester, is also present in the chromatogram to the extent of 60% of the dehydroabietate. This is fairly typical for a film of this nature.
The very small amount of pimarate is quite usual for a resin produced by various fir trees, and perhaps, that of _Abies alba_ Mill. (Strasbourg Turpentine) would be most relevant, bearing in mind the provenance of the instrument. Such a fir balsam would seem well suited as an instrument varnish since it would be quick to dry, whilst the dried film would be of pale colour and very tough. However, in this case, an _Abies_ resin can be ruled out, together with larch resin, such as Venice Turpentine, in view of the absence of the relevant neutrals. No triterpenoid resin was found in this specimen.
With the elimination of these possibilities, the chromatogram must be interpreted as representing a varnish with the main resin component from a _Pinus_ sp. source. In addition to this, there is evidence for a small amount of some form of copal from the Leguminosae, together with a little sandarac. The proportion of sandaracopimarate, relative to the other resin acids, is higher than normal for a Pinaceae resin and points to the addition of sandarac. The peaks due to acids in the general diterpenoid region, but with retention data which do not agree with the usual abietane, labdane and pimarane values, suggest the use of one of the lesser known copals. It is unlikely that these minor additions have any significant effect on the physical characteristics of the film.
A further sample of the varnish was leached overnight with benzene. No wax was detected in the extract. The insoluble material was saponified. The isolated acids were methylated and examined on an OV-' phase (2,3). The preponderance of azelate over saturated C_{16} and C_{18} acids, points to the use of drying oil. The palmitate to stearate ratio of 3.35 would suggest that it was walnut oil. The intensity of the chromatogram was not such as would indicate a large amount of oil had been added to the mixture. Normally, a pine resin would form a somewhat brittle film, ill-suited (on its own) to withstand the handling to which this type of instrument is subject. Probably, only just sufficient oil had been used to toughen and plasticise the varnish. Such a mixture would not be expected to be particularly quick drying, though no doubt the process would be hastened by the addition of lead dryers and by boiling.
It has been suggested that the old Brescian varnish and the later, coloured Cremona varnishes of the 17th. and 18th. Centuries were

gradually abandonned on account of their slowness to dry. From the middle of the 18th. Century onwards, they were progressively replaced by the rapidly drying spirit varnishes and the very tough 'run' copals. By the 19th. Century the recipes had been forgotten.

Samples from the Zanetto viola were treated in a similar manner to those from the Serafin, examined above. As in the previous case, there appeared to be some drying oil present in the varnish. A palmitate to stearate ratio of 3.3, once again, suggests the use of walnut oil rather than linseed. The chromatogram of the methylated ether/methanol solubles showed a pattern of peaks similar to that expected for an aged common turpentine (pine resin) film. In this case, however, there did not seem reason to suspect the addition of sandarac or any Leguminosae copals. The sandaracopimarate peak was closer to that normally encountered in pine colophony and there was no evidence for any acid components of the enantiomeric diterpenoid series. Of interest here was the preponderance of the oxidation product, 7-oxodehydroabietate, compared with dehydroabietate. This somewhat higher degree of oxidation, though by no means excessive, may account for the slightly darker hue of this varnish in comparison with that of the Serafin.
No trace of triterpenoid resins, such as dammars or mastic, were found.

Finally, the sample of varnish from the Tononi cello was submitted to analysis. This was a highly coloured varnish, unlike the two previous examples and was distinct in that, despite careful degreasing of the surface, the varnish still had a slightly matt, silky appearance. Once again, saponification and work-up of the fatty acid esters from the benzene insoluble material, revealed an addition of some drying oil. The ester ratio pointed to walnut oil as before (P/S = 2.97). In this instance, being a dark red-brown varnish, it cannot be that the paler colour, attributed to films of dried walnut oil, was a factor in the selection of this oil by the Master. Moreover, walnut oil is not such a rapid dryer as linseed. Rather, it was used because it was readily available, easily extracted and, presumably, cheaper in Italy than linseed oil. The ether solubles of a further portion, before methylation, showed a regular progression of odd carbon number hydrocarbons. One would estimate the peaks to represent carbon chain-lengths of the order of twenty, upwards. This clearly points to the use of beeswax. Bearing in mind that the surface had already been degreased, prior to analysis, it is not possible for this to represent remnants of later surface additions of wax polish. Indeed, this must come from a beeswax component incorporated within the body of the varnish layer or as a result of some form of priming layer. Further discussion of this will be made in the summary and conclusion below.
The methanol extract from the ether soluble material, after methylation, provided an unambiguous chromatogram. The identifiable peaks were assigned to the presence of dehydroabietate and 7-oxodehydroabietate, followed by lesser amounts of isopimarate, pimarate and sandaracopimarate. The dark nature of this varnish would seem not to be occasioned by the addition of strongly heated rosins. The

appropriate neutral components, formed during heating of this material, were found to be absent from the trace. Once again, the chromatogram was typical of a conifer resin and, in particular, a pine resin.
A portion of the methanol extract was further examined, following derivatisation to form the corresponding silylated products. These were distributed on a column coated with OV-101. A series of components were observed in the general triterpenoid region. This, coupled with the overall strength of the chromatogram, points to the presence of a little gum mastic or some form of dammar. Furthermore, several of the peaks had the same retention parameters as those from a 20 year old mastic film, which had been aged for fourteen years in the gallery laylight.
As yet, it has not been possible to identify the material responsible for the colour of this specimen. However, it does not seem to be a coloured resin, such as Dragon's Blood, but it does appear to be some form of organic dyestuff, adsorbed onto an inorganic base.

SUMMARY AND CONCLUSIONS:-

This brief study of varnishes from the three instruments, each thought to be from the early 18th. Century, has shown that fairly 'traditional' materials have been used. Both common turpentine and walnut oil would have been readily available, well-tried and cheap in the regions in which these instruments were constructed.
The Serafin varnish, in addition to oil and pine resin, contained small amounts of sandarac and perhaps a little copal, probably from some obscure African source. Small quantities would have little effect on the physical properties of the varnish.
The Zanetto varnish appeared to have only two components, pine resin and walnut oil. In this case, a little more oxidation of the resin acids had taken place. Possibly, this may account for the marginally darker colour of the varnish, but it must be said that we have no means of ruling out the use of amber in any of these varnishes. Certainly fused amber has always been said to impart considerable colour to varnish.
Amber has a very low amount of characteristic diterpenoids, the major component of which is Δ8-isopimaric acid. In favourable cases this might still just show up. However, if amber were incorporated with just one tenth of its weight of rosin, the latter's diterpenoids would completely swamp those of the amber.
The surface coating of the Tononi instrument was heavily coloured. Again, as for the Serafin and Zanetto varnishes, it was based on a pine resin with the addition of a little walnut oil to strengthen the film. A portion of gum mastic and, apparently, some lake-pigment, as yet uncharacterised, were present. Beeswax was incorporated with the varnish or possibly applied as a priming. It has been suggested that propolis may have been used in the violin varnishes of the Old Masters (4).
Propolis is a resinous adhesive collected by the bee and used to cement the comb. The precise nature of this material is uncertain,

but it may consist of polymerised terpene units. Certainly it seems to be contaminated with a proportion of wax. The presence of beeswax in the Tononi example might just be due to the application of propolis, though this seems a little unlikely. Unfortunately there is no means of telling, from analyses of composition of this sort, how the varnish was actually confected. So, this study does not permit us to say whether the oil was partially polymerised (sun-thickened or boiled) prior to addition of the resin component or whether the components were mixed and then subjected to moderate heating in the region of 200 - 250°C. Heating to this degree would not be expected to have a marked effect on the diterpenoid resin acid proportions, but would produce a darker varnish. The moderate toughness of these varnish samples, certainly suggest that the component oil was partly pre-polymerised.

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78/16/2

ETUDE DU TEMPS DE SECHAGE DU VERNIS PARALOID B72 SUR LES PEINTURES

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ETUDE DU TEMPS DE SECHAGE DU VERNIS PARALOÏD B72 SUR LES PEINTURES

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1

Résumé : Le temps de séchage du vernis Paraloïd B72 est étudié. Le vernis est mis en solution à 10% dans du toluène et du p-xylène marqués au carbone-14. Deux types d'étude sont entreprises, sur coupelle et sur peinture. Les éprouvettes de peinture sont prélevées sur une toile de 1895. Une quantité de 0,125 ml de vernis est déposée à l'aide d'une seringue sur chaque échantillon. La vitesse d'évaporation est mesurée et portée en graphique. Le temps de séchage est déterminé par la période de rétention du solvant et la quantité de solvant restant par le pourcentage de rétention.

Après restauration ou nettoyage, les peintures sont protégées par une résine diluée dans un solvant. Depuis 1973 Monsieur De Witte a généralisé l'emploi du vernis Paraloïd B72 à l'Institut. Le solvant utilisé était le toluène mais étant donné sa toxicité (1) et son odeur désagréable, il fut remplacé par le xylène.
Parmi les problèmes posés par le vernissage d'une peinture nous avons le vieillissement et le temps de séchage du vernis. Le changement de solvant, n'influençant que le temps de séchage, nous avons pensé qu'il serait intéressant de mesurer ce temps assez mal connu (2,3)
La méthode utilisée est identique à celle employée dans l'étude des effets des solvants sur les couches picturales (4)
Elle consiste à suivre l'évaporation du solvant, marqué au carbone-14, au cours du temps.
Nous avons entrepris deux types d'étude, sur coupelle et sur peinture afin d'essayer de mieux comprendre les phénomènes qui se passent sur les couches picturales.
Les solutions de vernis Paraloïd B72 à 10% sont préparées avec du toluène et du p-xylène marqués : 0,125ml sont déposés sur les échantillons et sur les coupelles à l'aide d'une seringue ; les éprouvettes sont prélevées sur une peinture datée de 1895 avec un emporte-pièce de 24mm de diamètre. La peinture comprend une couche de préparation (blanc de plomb), une couche picturale (bleu de Prusse) et un vernis (mastic) qui est enlevé à l'aide de chloroforme. Chaque type d'essai a été effectué trois fois afin de vérifier la reproductibilité

des résultats.

L'évaporation du solvant marqué au carbone-14 est suivie toutes les minutes et demies pendant 90 à 120 minutes et puis pendant 50 à 60 jours. Les résultats sont portés en graphique semi-logarithmique activité-temps. Pour les deux solvants, toluène et p-xylène, deux phénomènes se superposent :

1°) l'évaporation du solvant pendant la formation du film de vernis
2°) l'évaporation du solvant après la formation du film de vernis.

L'examen des graphiques nous permet de faire les constatations suivantes :

1°) la vitesse d'évaporation du toluène est supérieure à celle du p-xylène (fig.3)
2°) le solvant s'évapore moins vite sur la coupelle que sur la peinture (fig.1,2).
    Ceci peut être expliqué par le fait que le vernis suit les irrégularités de la peinture (5); la couche déposée à certains endroits est moins épaisse et l'évaporation du solvant est donc plus rapide.
3°) l'évaporation du solvant après formation du film de vernis est plus lente pour le toluène que pour le p-xylène (fig.1,2 et 3).
    Ce phénomène peut s'expliquer de deux façons :
    a) le p-xylène ayant deux radicaux méthyl, l'encombrement stérique est plus important et le solvant est moins lié au Paraloïd.
    b) le p-xylène a un moment dipolaire nul alors que celui du toluène est de $0,4 10^{18}$ e.s.u. Ce solvant a des liaisons dipolaires avec la résine et est donc plus retenu dans le vernis.
       Pour confirmer cette explication, il serait intéressant d'étudier l'o-xylène dont le moment dipolaire est $0,62 10^{18}$ e.s.u. Il devrait être plus lié au Paraloïd que le toluène et sa vitesse d'évaporation devrait donc être plus faible.

Le temps de séchage du vernis est déterminé par la période de rétention c'est-à-dire par le temps qu'il faut pour que la moitié du solvant présent dans le film de vernis se soit évaporée.
Cette période est déterminée à l'aide de la droite des moindres carrés calculées sur les mesures allant du deuxième au soixantième jour (7)

Essai	Solvant	Périodes, en jours
coupelle	Toluène	167
	p-Xylène	22
peinture	Toluène	73
	p-Xylène	9

Les périodes obtenues sont les moyennes des résultats calculés pour chaque essai.

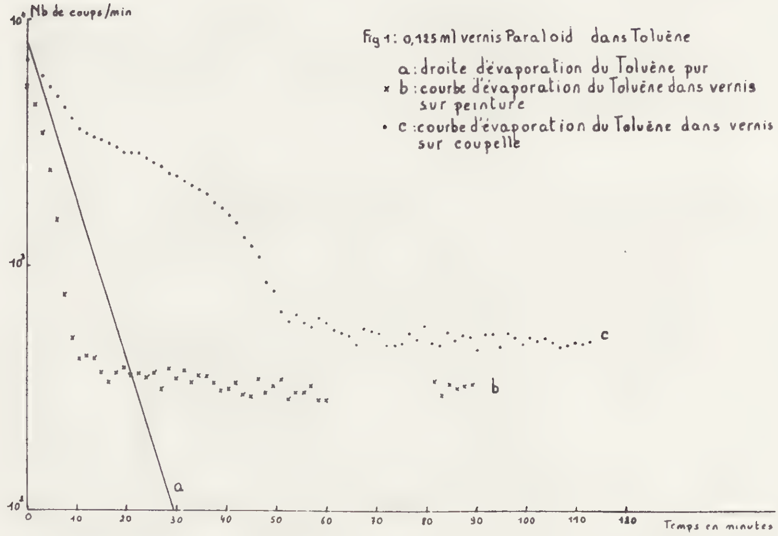
La quantité de solvant restant dans le film de vernis est déterminée par le pourcentage de rétention. Nous avons choisi de le calculer 10 jours après avoir verni l'échantillon. Le calcul tient compte de l'incertitude dans la diffusion des solvants ce qui explique un pourcentage minimum et maximum (8)

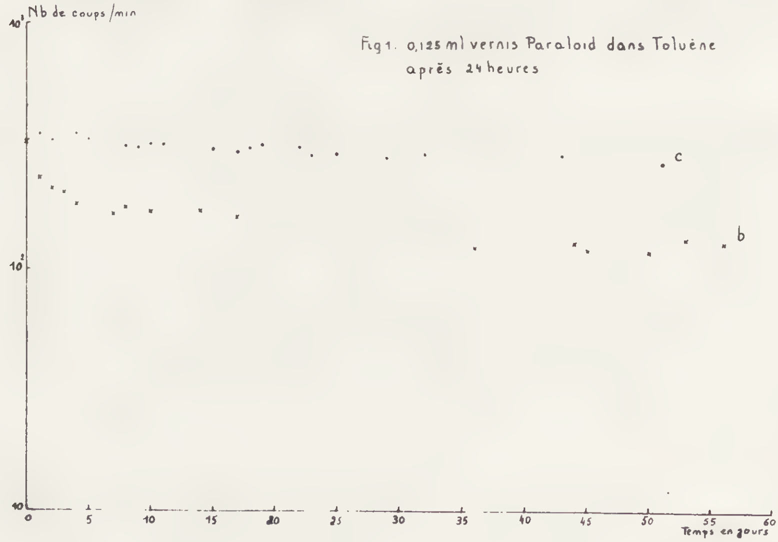
Essai	Solvant	Pourcentage de rétention
coupelle	Toluène	5 - 20
	p-Xylène	1,5 - 5
peinture	Toluène	3,5 - 13,5
	p-Xylène	1,1 - 5

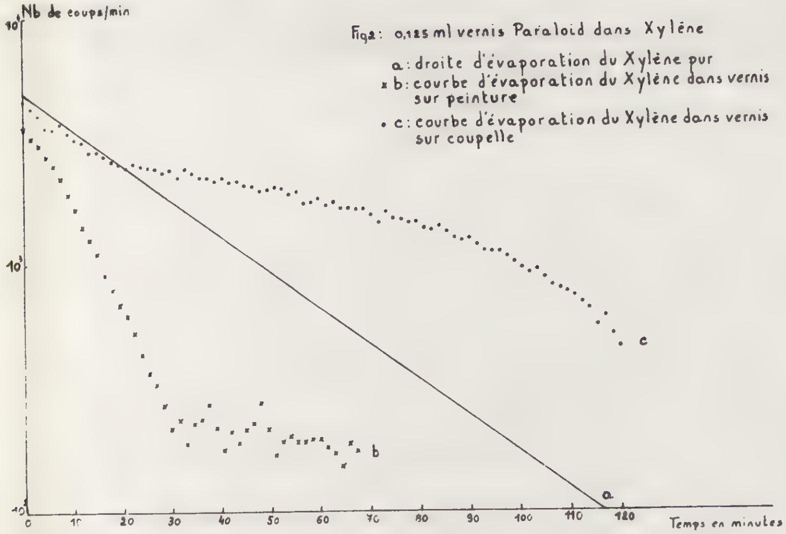
Les pourcentages obtenus sont les moyennes des résultats calculés pour chaque essai.

Conclusion

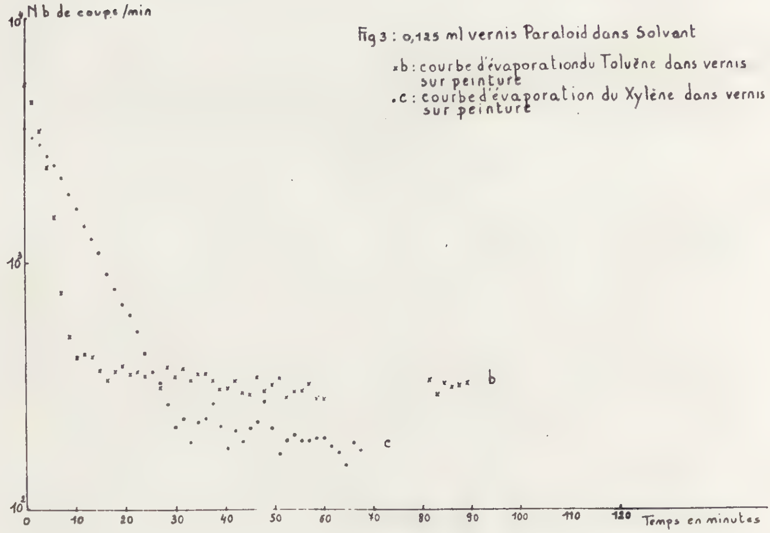
L'emploi du p-xylène nous a été imposé par l'achat du produit marqué au carbone-14.
Le xylène commercial est un mélange de o-p-m-xylène avec une prépondérance m-xylène. Ce mélange a un moment dipolaire égal à celui du toluène (6)
Etant donné nos remarques relatives aux liaisons du solvant avec la résine, nous pensons que le vernis Paraloïd devrait être préparé avec du p-xylène. Les perceptions sensorielles ne permettant pas d'estimer si un tableau verni est "sec", l'expérience nous montre que ce solvant est le mieux approprié étant donné sa période courte, son pourcentage de rétention peu élevé et sa vitesse d'évaporation pendant le formation du film relativement faible.

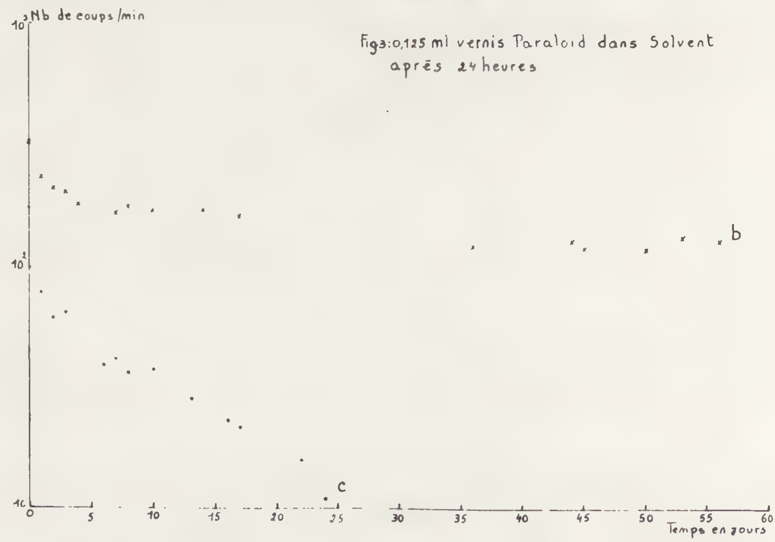

Nb de coups/min
Fig 1: 0,125 ml vernis Paraloid dans Toluène
a : droite d'évaporation du Toluène pur
× b : courbe d'évaporation du Toluène dans vernis sur peinture
• c : courbe d'évaporation du Toluène dans vernis sur coupelle
a
b
c
Temps en minutes


Nb de coups/min
Fig 1. 0,125 ml vernis Paraloid dans Toluène après 24 heures
c
b
Temps en jours


Nb de coups/min
Fig2: 0,125 ml vernis Paraloid dans Xylène
a: droite d'évaporation du Xylène pur
x b: courbe d'évaporation du Xylène dans vernis sur peinture
• c: courbe d'évaporation du Xylène dans vernis sur coupelle
c
b
a
0
10
20
30
40
50
60
70
80
90
100
110
120
Temps en minutes


Nb de coups/min
Fig2: 0,125 ml vernis Paraloid dans Xylène après 24 heures
c
b
0
5
10
15
20
25
30
35
40
45
50
55
60
Temps en jours


Nb de coups /min
10^4
10^3
10^2
Fig 3 : 0,125 ml vernis Paraloid dans Solvant
x b : courbe d'évaporation du Toluène dans vernis sur peinture
. c : courbe d'évaporation du Xylène dans vernis sur peinture
b
c
0
10
20
30
40
50
60
70
80
90
100
110
120
Temps en minutes


Nb de coups /min
10^3
10^2
10
Fig3: 0,125 ml vernis Paraloid dans Solvent après 24 heures
b
c
0
5
10
15
20
25
30
35
40
45
50
55
60
Temps en jours

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THE STRUCTURE OF 'OLD' AND 'NEW' PARALOID B 72

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ICOM Committee for Conservation

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Zagreb, 1978

THE STRUCTURE OF 'OLD' AND 'NEW' PARALOID B 72

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SUMMARY

Some years ago the physical presentation of Paraloid B 72 changed from white, irregular lumps into regular, transparant globules. Refractive index, viscosity grade and solubility properties indicate that the chemical composition of the new and the old B 72 could be different. This was confirmed by pyrolysis-gas chromatography and mass spectrometry. Both resins are copolymers of methyl acrylate and ethyl methacrylate, but the old B 72 contains 2 % more methyl acrylate than the new. Since this small change in composition results in some distinct changes in physical properties of the resins it is advised to repeat some of the aging tests carried out before on the old B 72.

I INTRODUCTION

Paraloid B 72 is used for many years in conservation as picture and metal varnish (1,2,3), as consolidation agent (4) and for paint fixing (5). Intensive aging tests by Feller (6) showed that it is one of the most stable resins used in the restoration of works of art.

About 3 years ago, the aspect of Paraloid B 72 changed. Where it used to be furnished as white, irregular lumps, it now appears as very regular, transparant globules.

Besides the aspect, the only difference one notices immediatly is that new Paraloid B 72 (B72 N) is completely odourless. The old Paraloid B 72 (B72 O) had a ~~slig~~ slight smell of acrylate- or methacrylate monomer. We wondered if with the change in aspect there was also any change in chemical structure. Rohm and Haas Belgium confirmed there was none, and that only the "physical presentation" was changed. The manufacturer also stated that "by a perfectionated fabrication technique, a compound with lower percentage in residual free monomer was made".

In order to be sure the two resins are really identical, some physical properties such as refractive index, viscosity grade and solubility in ethanol were measured. IR spectroscopy, NMR spectroscopy and pyrolysis-gas chromatography followed by mass spectrometry were also used to reveal the exact structure of both polymers.

II RESULTS AND DISCUSSION

1. Refractive index :

The refractive index was measured with a Fisher Refractometer. A solution of the resin in toluene is applicated on the prism. After evaporation of the solvent the refactive index can be measured. As can be seen in table 1, the refractive index of B72 O is slightly lower than that of B72 N.

2. Viscosity grade :

The viscosity grade, as defined by Feller (7), was measured with a Höppler viscosimeter. As can be seen in table 1, the viscosity of B72N is higher than that of B72 O. This indicates that the molecular weight of the latter is lower.

3. Solubility in ethanol :

Solubility tests in cold and warm 95 % ethanol show that there must be a difference in chemical structure between B72 O and B72 N. B72 O is soluble in ethanol at 65°C, but precipitates by cooling. B72 N is soluble in cold as well as in warm ethanol.

4. Infra-red spectroscopy :

IR-spectroscopy could not reveal any difference between the two resins : both IR-spectra are identical.

5. Nuclear Magnetic Resonance spectroscopy :

NMR-spectra of the two polymers were taken on a Varian 90 MHz spectrometer in ortho dichlorobenzene at 85°C. By comparing the peaks at 3.6 δ (O-$\underline{CH_3}$) and at 4.15 δ (O-$\underline{CH_2}$-CH_3) the ratio ethyl ester/methyl ester can be calculated. In table 1 it can be seen that this ratio is greater for B72 N than for B72 O. This allows to conclude that B72 O contains 2 % more methyl ester-groups than B72 N. With this method it is not possible to reveal if we have to deal with acrylic- or methacrylic esters.

6. Pyrolysis-gas chromatography- mass spectrometry :

As the former results show that there must be a difference in chemical structure between B72 N and B72 O, the resins were analyzed by pyrolysis-gas chromatography-mass spectrometry. Pyrolysis is often used for the identification of acrylic- or methacrylic polymers, because the pyrolyzates are mainly monomers, dimers and trimers (8). The pyrolyzing unit was a Varian Pyroprobe Model 9250. The pyrolyzing temperature was 500°C ; the pyrolyzing time 5 sec. The degradation products were analyzed on a Varian 4000 gas chromatograph, equiped with a 50 m capillary column, coated with Carbowax 20M. Mass spectra were recorded with a Finnigan 3200 mass spectrometer,

equiped with a 6000 Data system. The pyrogram of B72 N is shown in fig. 1.The identification of 13 peaks is summarized in table 2.

Analysis of the results shows that the pyrogram can be devided into 3 parts :

A- peaks 1-3 : monomers and traces of residual solvent
B- peaks 4-7 : dimeric degradation products
C- peaks 9-13: trimeric degradation products
The exact structure of the dimeric and trimeric products is still under investigation and will be published later.

This results allow to conclude that B72 N is a copolymer of ethyl methacrylate (EMA) and methyl acrylate (MA). This is confirmed by pyrolysis of a polymer, synthesized by copolymerization of EMA and MA. The pyrogram of the latter is identical to that of B72 N.

6.2. <u>Comparision of the pyrograms of B72 N and B72 O</u> :

Pyrolysis of the two resins gave similar pyrograms. However, the relative peak intensities show marked differences. As can be seen in fig. 2, the relative peak intensity of peak 9, a trimer of MA, is higher in B72 O than in B72 N. This means that B72 O contains more MA-triads and consequently that there is more MA in the B72 O than in the B72 N, which is in agreement with the results obtained from the NMR-spectra. The higher content of MA also explains the differences in refractive index and solubility between B72 O and B72 N. In table 1 the characteristics of both polymers are compared with these of pure poly-EMA (PEMA) and pure poly-MA (PMA). As can be seen in this table, the refractive index of B72 O is identical to this of PMA. The higher amount of EMA in B72 N causes a shift of the refractive index towards this of PEMA. The same effect occurs with solubility. PEMA is soluble in ethanol at 65°C and stays in solution by cooling.
So does B72 N. B72 O is, just as PMA, insoluble in cold ethanol.

III CONCLUSION

The analysis of old and new Paraloid B72 allows to conclude that there is a small but definite difference between the two resins. Both are copolymers of methyl acrylate and ethyl methacrylate. In the new B 72 the ratio EMA/MA is 70/30, in the old is 68/32. This small difference in composition influences the solubility in cold ethanol.

Altough we do not believe that there is any influence on the stability of the resin, it should be worthwhile to repeat some aging tests.

Once again the restoration world has to deal with a change in composition of a very valuable product, without any warning of the manufacturer. This proves that restorers should always be vigilant when there is any change in the physical presentation of one of their products. It is the authors opinion that it is absolutely necessary that the chemical composition of the commonly used materials in restoration is known in detail so that in the future, changes in composition can be recognized. Only in this way will it be possible to avoid difficulties which arise when manufacturers decide to change the composition or to stop the fabrication of their products.

	PMA	B72 O	B72 N	PEMA
Refractive index	1.479	1.479	1.481	1.485
Viscosity grade	-	34.74	42.08	-
Solubility in				
warm ethanol	-	+	+	+
cold ethanol	-	-	∓	+
ethyl/methyl ester	-	68/32	70/30	-

Table 1 : Comparision of physical properties and composition of PMA, B72 O, B72 N, PEMA

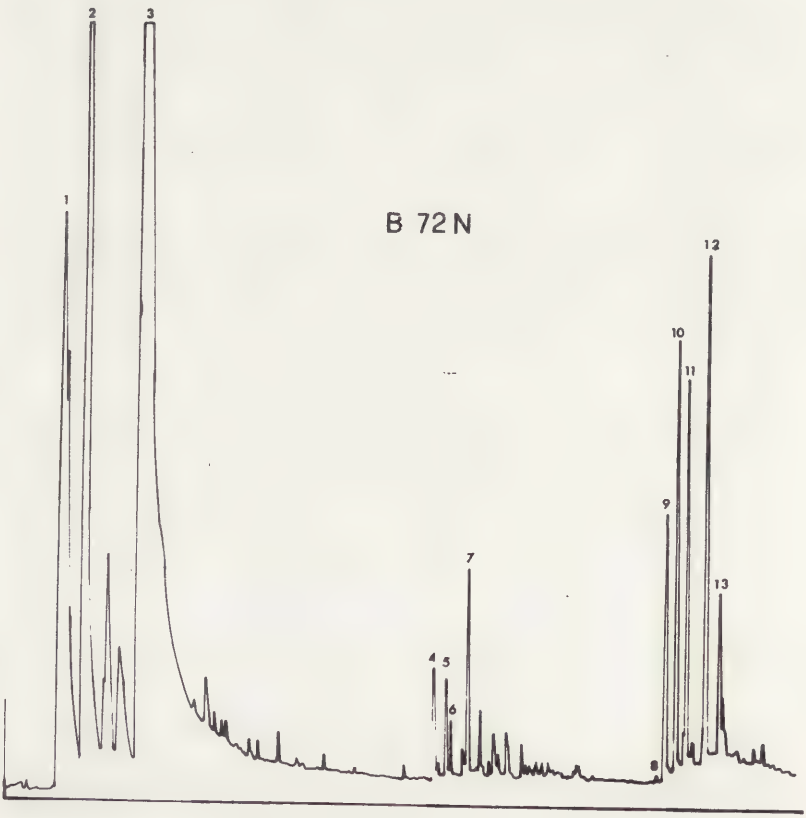

Figure 1 : Pyrogram of B72 N

Peak number	mol. weight	identification
1	92	toluene : residual solvent from synthesis
2	86	methyl acrylate
3	114	ethyl mehatcrylate
4	172	dimer of MA
5	188	dimerisaton product of MA + EMA
6	186	dimerisation product of EMA
7	200	dimer of EMA
8	198	phenyl benzoate : decomposition product of the initiator
9	258	trimer of MA
10	286	trimer of 2 x MA + 1 x EMA
11	286	trimer of 2 x MA + 1 x EMA
12	286	trimer of 2 x MA + 1 x EMA
13	314	trimer of 1 x MA+2 x EMA

Table 2 : pyrolyzates of Paraloid B 72

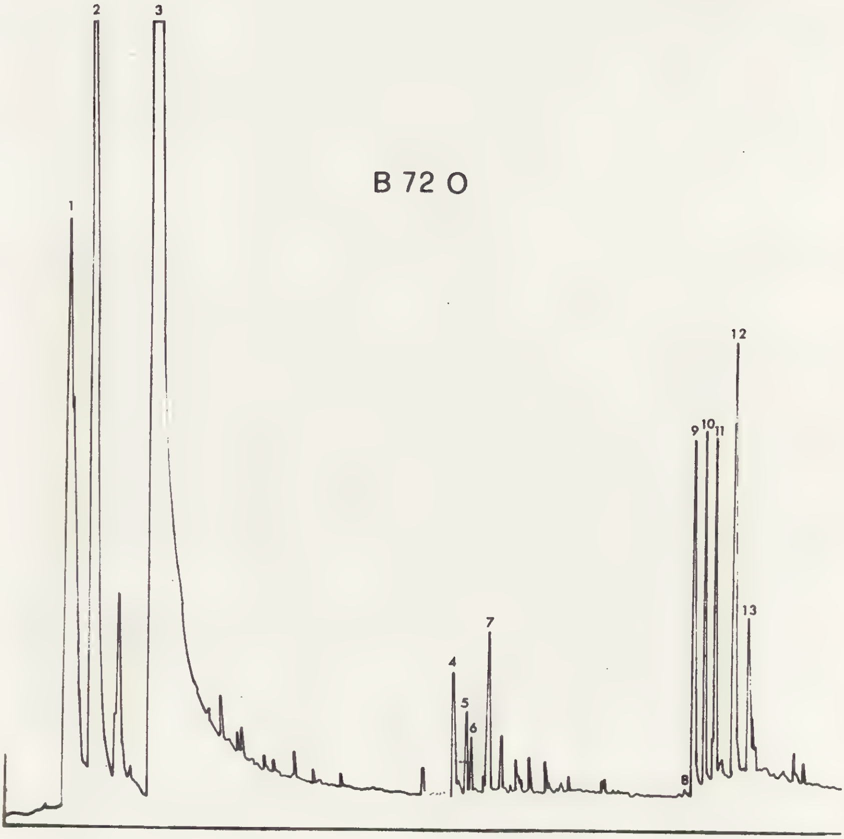

Figure 2 : Pyrogram of B72 O

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STANDARDS IN THE EVALUATION OF THERMOPLASTIC RESINS

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STANDARDS IN THE EVALUATION OF THERMOPLASTIC RESINS

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ABSTRACT

A standard method is proposed for evaluation of the photochemical stability of resins and polymers intended for use in long-term conservation practices. The method is based on the International Standards Organization's Recommendation R105 blue-wool fading scale. In addition, three different types of polymers of known composition are proposed as standard reference materials (materials standards) and two methods are recommended for reporting key properties of polymers in a standard manner.

INTRODUCTION

In the search for new and highly stable organic coatings for use in conservation, the conservation profession has as yet no generally accepted standards for materials evaluation or for laboratory test procedures. The world of conservation needs not only recognized standards, but also a common technical language with which to speak of these problems. The Materials Center has for a number of years been devoting special attention to the selection of methods appropriate for evaluating the long-term stability of polymers and resins. At the last triennial meeting, a standard of "temporary use" for conservation materials was defined (less than six months) and three standards of photochemical stability were recommended (Table 1).[1] Since that date, a review has been published concerning the problems of accelerated photochemical-aging tests.[2] At this 1978 meeting of the working group, additional material standards and several test methods will be proposed.

LIMITED NUMBER OF CLASSES OF STABILITY USEFUL

The range of organic materials that modern chemistry can offer the conservator is very great. Synthetic polymers may be encountered that have 10, 100, perhaps 1000 times the stability of traditional materials. A "classification" scheme, therefore, must span more than a decade of relative stability.

The basis of the standards of photochemical stability proposed in 1975 (Table 1) is the International Standards Organization's R105 blue-wool scale.[3] The proposed classes were selected so that each higher classification was about five times greater than the lower: class C less than 20 years, class B greater than 20 years,

class A2 greater than 100 years, and class A1 greater than 500 years.

TABLE 1

Standards of Intended Use and Photochemical Stability for Materials in Conservation

Class	Classification	Intended Useful Lifetime	Approximate Equivalent Standard of Photochemical Stability
T	Materials in Temporary Contact	less than 6 months	-
C	Unstable or Fugitive	less than 20 years	BS1006* Class 3 or less
B	Intemediate	(20-100 years)	(Between Class 3 and 6)
A	Excellent	(A2?) greater than 100 years	greater than BS1006* Class 6
		(A1?) greater than 500 years	5x more stable than A2

* British Standard BS1006:1971 is equivalent to the International Standards Organization (ISO) Recommendation R105.

A larger number of "classes" of stability could be chosen - there are, after all, eight blue-wool standards. However, three basic classes should prove adequate and should do much to minimize disputes regarding "borderline" cases of stability.

MINIMUM PHOTOCHEMICAL STABILITY OF MATERIALS SUITABLE FOR CONSERVATION

Modern chemistry has given us polymeric materials that possess sufficient photochemical and thermal stability that they can be expected to maintain their essential physical and chemical properties for many hundreds of years under the relatively mild conditions represented by the indoor climate of museums. The proposed general class "A", thus, in a sense, represents only a minimum standard because of the difficulty of predicting a much longer lifetime with assurance. If one wished to refer to materials that might meet a higher standard, the author has suggested "A1" to be used to designate materials that promise a useful lifetime of more than 500 years; A2, for those likely to be stable between 100 and 500 years. Indeed, once the field of conservation begins to consider the most stable types of modern

materials, fluoropolymers, for example, a high classification such as A1 may prove to be necessary.

The conservator's usual requirements for (a)"reversibility" (b) applicability at low temperatures and (c) removability in relatively "mild" solvent-systems have generally served to limit the number of materials, particularly thermoplastic resins, that can meet the proposed class A standard. Thus, although many fluoropolymers possess outstanding durability, their application and removal present problems that have thus far limited their use by conservators.

What, then, is the definition of a material that is of "sufficient photochemical stability that it can be used in conservation"? In its search for new organic coatings and adhesives to be used in conservation, the Materials Center at Carnegie-Mellon Institute has considered only class A materials (Table 1). The basic objective has been to select materials that could be expected to suffer a loss of no more than about 20% of their essential properties in 100 years exposure under normal museum conditions.

The ability of a substance to meet such a requirement cannot be estimated with complete assurance on the basis of accelerated aging tests. However, the defined standard based on ISO blue-wool standard No. 6 provides a readily available, well-recognized standard that will allow the conservator to select materials that should come close to meeting, if not exceeding, the objective of a minimum of 100 years of stability. It can be demonstrated that standard No. 6 will only fade to Geometric Grey Scale contrast of 3 (British Standard BS2662) after about 213 million lux hours (20 million footcandle hours) of "daylight" fluorescent lamplight under average room conditions. Assuming annual exposures on museum walls to be 1 to 1.5 million lux hours, [4] it seems reasonable to propose that a class A material should be at least as photochemically resistant as an ISO R105 blue-wool standard No. 6.

METHOD OF USING STANDARDS OF PHOTOCHEMICAL STABILITY

The use of the standards proposed in Table 1 is as follows: If one wishes to evaluate a resin, paint or pigment as to (a) whether it might be expected to maintain its desirable properties for no more than a decade or two on a well-illuminated museum wall or (b) whether it may be expected to maintain its integrity for perhaps more than a century, the test specimen can be placed on accelerated photochemical exposure along with a set of the ISO R105 blue-wool cloths and compared to their behavior. The blue-cloths act as an exposure monitor. Whatever physical property is of interest and is known to be affected by exposure to the normal light sources in museums and archives, it can be monitored in this manner. Thus, whether the physical property be brittleness, loss of solubility, discoloration, cracking or fading - if unsuitable deterioration fails to appear in

the test specimen before blue-cloth No. 6 noticeably fades - then the assumption can be made that the material under test has excellent photochemical resistance with respect to the particular physical property under consideration. In the case of Paraloid® B-72, for example, neither yellowing, cracking nor marked loss of solubility occurs in the usual xenon-arc fadeometer or "daylight" fluorescent lamp exposures by the time ISO R105 blue-cloth No. 6 has significantly faded.

PROBLEMS POSED BY MATERIALS OF INTERMEDIATE STABILITY

It is relatively easy to determine those materials that are highly unstable. Class A materials, on the other hand, usually require many months of "accelerated aging" before deterioration can be demonstrated. Thus, the more stable a substance is, the longer the test period that is generally needed to demonstrate its resistance to deterioration.

The usual alternative to waiting a long time is to increase the severity of the exposure. However, increased temperature and intensity of light often give false indications of what will occur under natural conditions of aging. The author has reported in one example that the high temperature of specimens in the usual carbon-arc fadeometer favors crosslinking of isobutylmethacrylate polymers, whereas at a lower temperature, chain breaking is the major change that occurs instead of crosslinking.[5]

The investigator usually attempts to circumvent the many doubtful factors involved in the application of accelerated test conditions by comparing new products to the old - the old serving as a "control" sample. This procedure is most successful when the new materials far outlast the old; that is, when the new is obviously better than the old.

Suppose, however, that a material fails under accelerated photochemical testing, but proves to be almost as good as the control. This poses a problem for the investigator because he has no assurance that it would not "pass" - would not be better than the control - under milder conditions. Consider, further, the following results from an accelerated test: product X, previously shown to be a class C material, fails in 10 ± 2 hours, product Y (under study) fails in 70 ± 5 hours, and Paraloid® B-72, the "control", a class A material, fails in 110 ± 5 hours. From previous studies, it is known that Paraloid®B-72 is considerably better than the minimum for a class A material. The question arises: should one reject product Y as "not being class A"? While product Y clearly exhibited lower stability under accelerated aging than the control, it is seven times more stable than product X and may, therefore, be in photochemical class A (Table 1) even though it is significantly less stable than the control. An example of such a borderline case,

difficult to classify with assurance, is the evaluation of the stability of ethylenevinylacetate copolymers reported to this working group at the Venice meeting in 1975. (1)

FACTOR OF SAFETY IN SELECTION OF MATERIALS OF CLASS A PHOTOCHEMICAL STABILITY

Although product Y in our example obviously is not as stable as the control under accelerated test conditions, it may be of sufficient stability for use in conservation, particularly under the mild conditions of exposure encountered in a museum. Coming back to the question, then, of what materials can be judged to be "sufficienty stable for use in long-term conservation practices", several factors are evident. First of all, it is relatively easy to determine those materials that are unstable. Secondly, materials of outstanding stability can be selected with reasonable confidence; the Materials Center has selected Paraloid® B-72 for a standard of an excellent (class A) thermoplastic polymer that is initially soluble in solvents equivalent to or milder than xylene and which retains a high degree of solubility during long periods of exposure. However, the determination of "acceptable" materials exhibiting stability less than Paraloid® B-72 - that is, the establishment of the "lower limit of acceptable stability" - is open to question. (6)

The problem of establishing minimum performance characteristics of a material that still represents sufficient stability to be safe for use in long-term conservation treatments will remain a challenging one. The Materials Center has sought to circumvent this problem by selecting a few standard materials that are considered to be significantly more stable than the absolute minimum. Such a decision in choosing a practical working lower-limit of acceptability for a material in conservation can be compared to the engineer's procedure of employing a factor of safety in designing mechanical devices: an attempt is made to provide a degree of strength (photochemical resistance or other vital physical or chemical characteristic) in excess of what is estimated to be the absolute minimum requirement. Helmut Ruheman expressed very much the same principle many years ago in his effort to specify a "factor of safety" in the selection of solvents for the removal of varnishes. (7)

Conservation specialists should be able to agree upon a few materials that are of excellent stability and also to identify a few that are obviously of intermediate stability. Hopefully, it should not be necessary to argue at length about the acceptability of products of intermediate stability - materials that in effect are "good enough". In conservation practice, "good enough" should not be the final goal; the search must be for the most stable, the very best, materials available.

CONTROLS: MATERIALS STANDARDS

Because accelerated-aging tests involve uncertainties when attempts are made to "extrapolate" the results to predict behavior at room temperatures, reference standards, or "controls" are usually employed. Several materials have been suggested by this laboratory in the past as controls [2] and the reasons for suggesting them will be reviewed here again.

Suggested Principal Standards: (1) the ISO R105 blue-wool fading standards represent internationally recognized, readily available and reasonably priced standards of photochemical sensitivity. These are proposed as principal control samples to measure photochemical exposure. [1][2]

(2) Paraloid (Acryloid)®B-72 is a class A material of excellent photochemical stability. The very slow change in solubility of this polymer in a carbon-arc fadeometer has been reported [8]; its ease of removal relative to dammar, mastic and polycyclohexanone resins measured [1][9]; its tendency to chain break relative to polyvinylacetate demonstrated [1][5]; and its lack of brittleness relative to polymers of lower viscosity grade pointed out. [10] The viscosity grade of Paraloid® B-72 is about 29 centipoises (for definition of viscosity grade, see below). [10]

Suggested Secondary Standards: (3) Polyvinylacetate homopolymers have long been made in similar molecular-weight grades throughout the world. [10] For convenience, one grade, - that of viscosity grade 80, corresponding to Union Carbide AYAF, Airco Vinac® B-15, Mowolith 50, Vinavil K50 and Vinnapas UW1 - could be selected as a principal control polymer if this is considered desirable. Whenever any particular polyvinylacetate or similar thermoplastic resin is used, however, its viscosity grade should be identified. It is even possible to specify the viscosity grade of the resin in a polymer emulsion, although more effort is involved to obtain this information than in the case of the lower molecular-weight resins supplied as 100% solids. To the best of the author's knowledge, polyvinylacetate homopolymer is a class A material.

(4) Poly(butylmethacrylate) - iso, normal or copolymers thereof- can be prepared by refluxing overnight in toluene with about 0.5% benzoyl peroxide as a catalyst based on the weight of monomer. The product that is precipitated by adding alcohol, subsequently vacuum-dried or redissolved in a suitable solvent, corresponds closely in photochemical stability to the long known commercial products, Elvacite® 2044, 2045 and 2046 (du Pont). These polymers crosslink and lose their solubility at a known rate under near ultraviolet radiation. The quantitative measurement of their loss of solubility, as shown in Figure 1, can serve as a useful standard of photochemical stability for a class B material. The method illustrated in Fig. 1 has previously been proposed as a

standard procedure for reporting the loss of solubility of polymers.[6]

One of the major reasons for proposing these three types of polymers as materials standards is that their composition is known and, if required, they can be prepared from the monomers in the laboratory in viscosity grades that correspond as closely as desired to the commercially available products.

A WORD OF CAUTION: MATERIALS STANDARD VS. SUITABILITY IN SPECIFIC APPLICATIONS

The above standards represent reasonably well-characterized materials of tested stability; in themselves they exhibit class A or B photochemical stability. Such a classification does not imply that for a particular use - as an adhesive, paint, consolidant or clear protective coating - they may fail more rapidly in a given situation than some other material. No one substance is universally applicable to every conservation problem. The emphasis is on the stability of the material, not the system. These particular polymers and the blue-wool standards are recommended as an initial set of reference materials that are reasonably easy to obtain and that can be expected to have reasonably well-defined properties. Other materials undoubtedly will be proposed in the future and investigators working in the field will want to evaluate such new proposals as to their suitability and appropriateness. However, it is hoped that the several materials referred to here will prove to be a useful initial set of reference "control" standards in testing and evaluation of conservation materials and methods.

STANDARD LABORATORY TEST METHODS

The viscosity grade of a polymer and the "mildest" solvent that will dissolve it are useful properties to specify. The following two methods of measuring these key properties are simple to employ.

Viscosity Grade of Polymers: The average molecular-weight grade of many polymers can be conveniently indicated by reporting their "viscosity grade", the viscosity of a 20% solution of the resin in toluene at 70°F (21.1°C).[10] For very high molecular weight materials, the viscosity of a 2% solution in toluene, water, or if necessary, other suitable solvent can be used.

Series of Solvents of Increasing "Strength": A key property of a thermoplastic or lightly-crosslinked polymer is the "mildest" solvent that will either dissolve or swell the coating. In 1972, mixtures of cyclohexane, toluene and acetone were proposed that would provide a series of solvents of regularly changing "strength" based on Teas' triangular-coordinate plots of three parameters.[11][12] This series of solvent-mixtures, given in

Table 2, has been used to compare the rate of loss of solubility of the following natural and synthetic resins: dammar, mastic, Resin AW-2®, Ketone Resin®, MS-2A®, polyvinylacetate Gelva® B-15 and Paraloid® B-72. (9) The essential results of the testing program on these resins were summarized in Figure 4 in the author's 1975 report to this working group of the ICOM Committee for Conservation. (1)

TABLE 2

Solubility Parameters, f_d (Teas), of Mixtures of Cyclohexane, Toluene, and Acetone Having Systematically Increasing Solvent Power

Mixtures: Volume Percent of			Approximate
Cyclohexane	Toluene	Acetone	Value of f_d (Teas)
100	0		96 (weak)
75	25		92
50	50		88
25	75		84
	100		80
	87.5	12.5	76
	75	25	72
	62.5	37.5	68
	50	50	64
	25	75	56
		100	47 (strong)

Solvents having both very high or very low solubility parameters relative to a given resin tend not to dissolve it. The solvent mixtures listed in Table 2 will usually be used to determine the lower or "milder" limit of a solvent system that has the ability to dissolve a resin or film. This is illustrated in Figure 2; the open circles are solvent systems that will not dissolve polyvinylacetate; the closed circles are within the area of solvent power that will dissolve this polymer. The solvent mixture that has just enough toluene (in this case) to dissolve the resin can thus be determined with considerable precision.

It is proposed that the solvent mixtures given in Table 2 be used as a convenient standard series by which to specify the mildest solvent system that will dissolve or remove a fresh or aged resin. For convenience, the stepped series of about ten solvents in Table 2 can be used. However, for precise measurements, the exact composition that just succeeds in dissolving the resin, or in swelling it to a given degree, can be determined. The principal

standard for reporting solubility would be a diagram of the complete solubility characteristics on the Teas' diagram.

CONCLUSION: SUMMARY OF SUGGESTED STANDARDS

The author proposes that, during the next three-year period, the members of the working group on protective coatings concentrate on the problem of establishing standards of materials and of test procedures that can be used to coordinate the international effort to develop durable new materials for conservation. The following are suggested as material standards:

Principal Standards

ISO R105 Blue-Wool Fading Standards
Paraloid (Acryloid)® B-72 (a class A material)

Secondary Standards

Polyvinylacetate (a class A material)
Polybutylmethacrylate (iso, normal or copolymer) (a class B material)

The following are suggested as standard laboratory test methods:

Specification of photochemical stability: the three classes given in Table 1.

Specification of viscosity grade: viscosity of a solution at 70°F (21.1°C) preferably at 20% concentration in toluene.

Minimum strength of solvent to dissolve or remove resins: Use of mixtures of cyclohexane, toluene and acetone.

As the number of technical laboratories devoted to the study of conservation materials grows, there is a corresponding increasing need for standard methods for use in describing the characteristics of the many polymers and resins which might be considered.

It is hoped that members of the working group will give immediate consideration to these proposed standards or to others which may be suggested.

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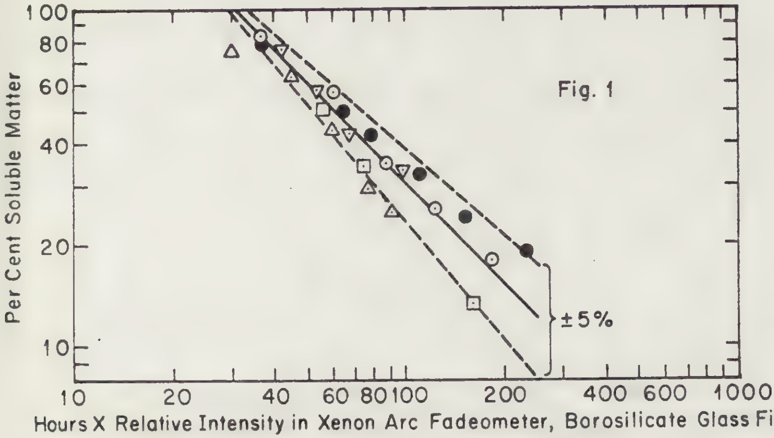
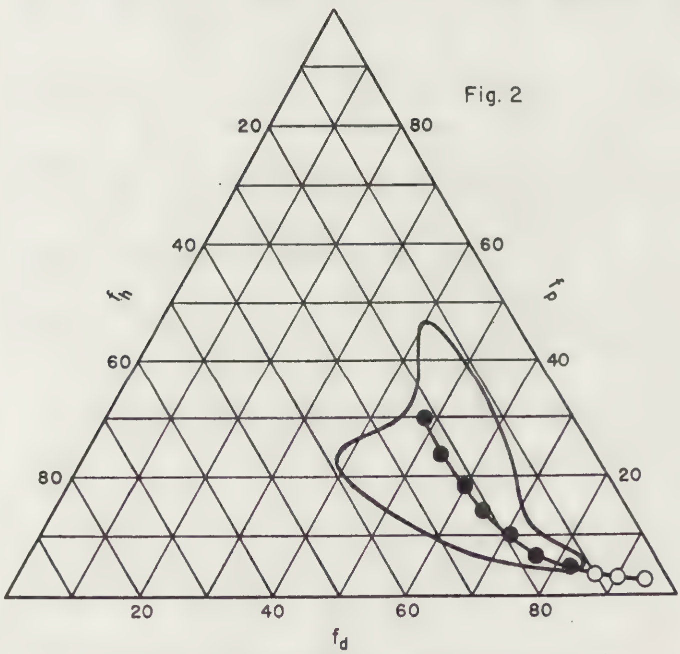


Behavior of Six "Control" Samples of Elvacite ® 2046
(Butyl Methacrylate Copolymer) Over Seven Year Period



Solubility Characteristics Polyvinylacetate

DAMMAR AND MASTIC INFRARED ANALYSIS

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DAMMAR AND MASTIC INFRARED ANALYSIS

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Abstract

Infrared spectra for seven specimens of dammar and mastic were obtained with a Digilab Model FTS-14 Fourier transform infrared spectrometer. Though significant differences were observed among the samples, considerable additional research will be required before the causes of these differences are fully understood.

In 1954 in a paper by the same name Feller commented that "Infrared analysis is known not to be sensitive in the analysis of trace materials and is not particularly adapted to the study of extensive mixtures. In the examination of materials used in the fine arts, these factors will limit the effectiveness of the method..." (1). These comments, which were based on the observations that the infrared spectra of good and poor grades of mastic and dammar were practically identical, spectra of recent and old dammars were practically the same, and spectra of fresh and aged resins were quite similar, were realistic and valid at the time because the quality of the spectra obtainable then was severely limited by the quality of the instrumentation. However, the fairly widespread belief that infrared spectroscopy is of little use for studying complex mixtures must now be modified. Much better instrumentation is now available.

Some examples of infrared spectra of resins are shown in Fig. 1. The resins were dissolved in chloroform and films were cast on KCl plates. The spectra were recorded with a Fourier transform spectrometer, Digilab Model FTS-14 (2,3). As with other spectra of similar resins (4,5), there are great similarities. However, the quality of the spectra is now so high that numerous differences are discernible. Arrows point to some of the features which distinguish the spectra. The major absorptions may be similar, but there are differ-

ences in relative band intensities, the breadth and contours of bands, shoulders, etc.. Scale-expanded segments of spectra (Fig.2) show that there are also significant differences in the 1500-800 cm^{-1} region. Moreover, as shown in Fig.3, there are also differences between the spectra of a fresh and an artificially aged sample.

There is thus a wealth of data which can and does fingerprint each sample, although at present this proves to be an embarassment of riches because not enough work has been done as yet to determine the causes of the differences. However, the spectra are of such high quality that each trace can be used as spectral signature, and the now readily discernible differences hold out the promise that it will become possible to study the effects of aging, exposure to light, the nature and source of the resin, etc.. The techniques can, of course, be extended to other materials.

It seems pertinent to remark that the infrared analysis of trace materials and the study of extensive mixtures basically involve the same thing: recording spectra with great precision and high resolution. That can now be done. Consequently, infrared spectroscopy can be expected to find wider applications and become more useful than in the past.

Acknowledgement

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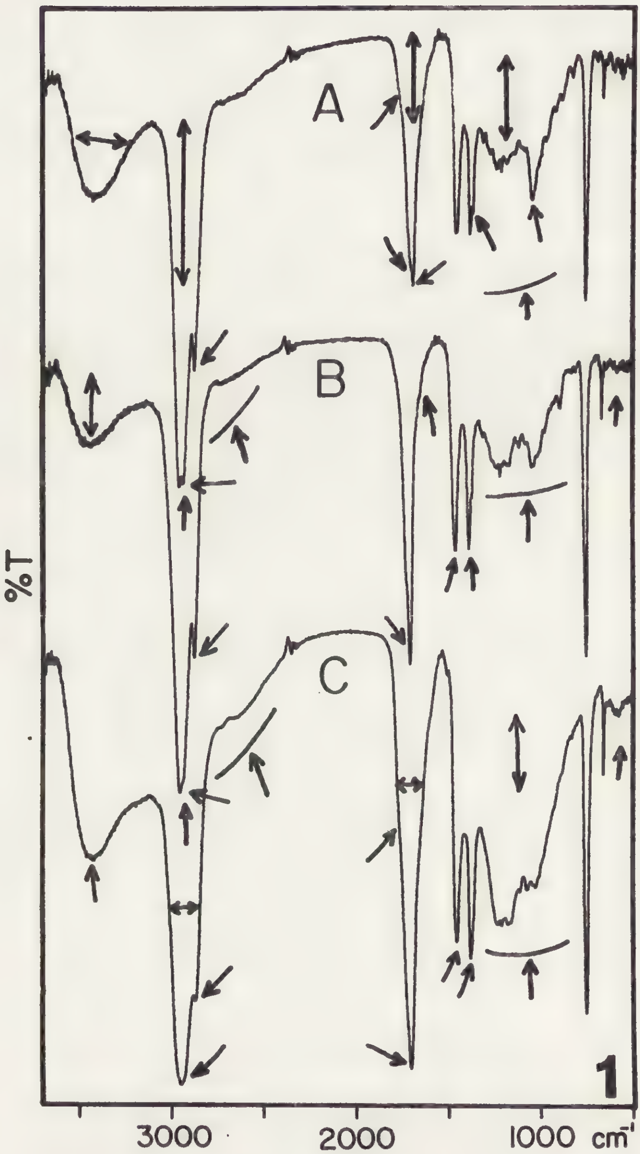
Figures

Fig. 1. Infrared Spectra of Dammar and Mastic. A: Sal Dammar; B: Dammar, Fezandie and Sperrle, April 9, 1958; C: Mastic, 1920-1923.

Fig. 2. Segments of Spectra of Dammars and Mastics. A,B,C,: as in Figure 1.; D: Mastic, Fezandie and Sperrle, June 5, 1962; E: Gum Dammar, Singapore Lumps, Fisher Catalog No.G101; F: Gum Dammar, Fezandie and Sperrle, April 1962; G: Batavia Dammar, 1920-1923.

Fig. 3. Spectra of Natural and Aged Dammars. A sample of dammar (Fezandie and Sperrle, April 9, 1958), upper trace, was exposed to the radiation from a mercury vapor lamp for two hours at room temperature, lower trace.


A
B
C
%T
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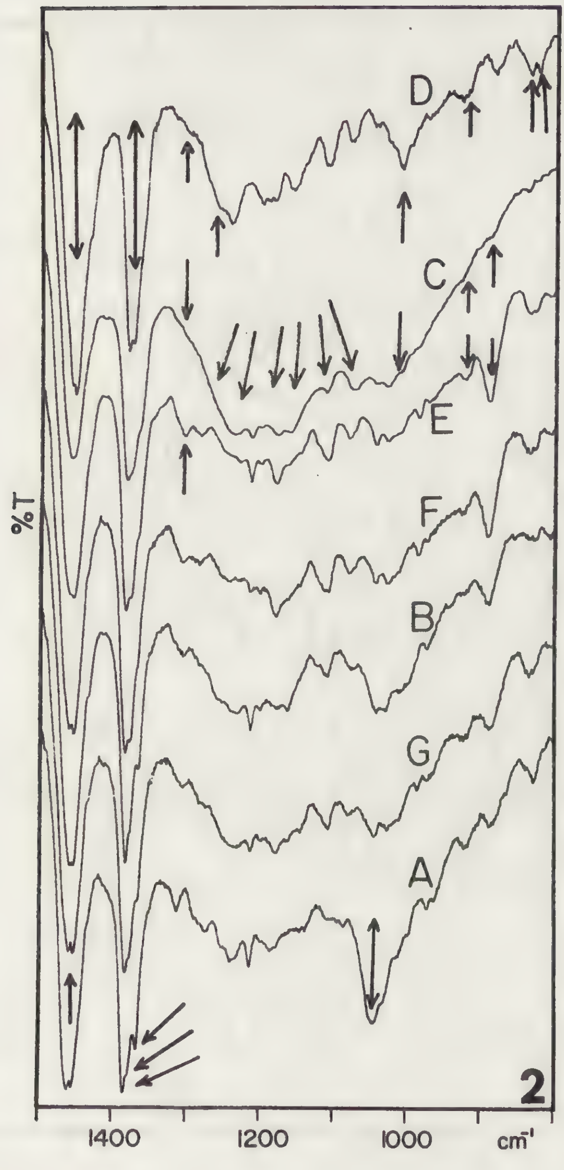
3000
2000
1000 cm⁻¹



%T
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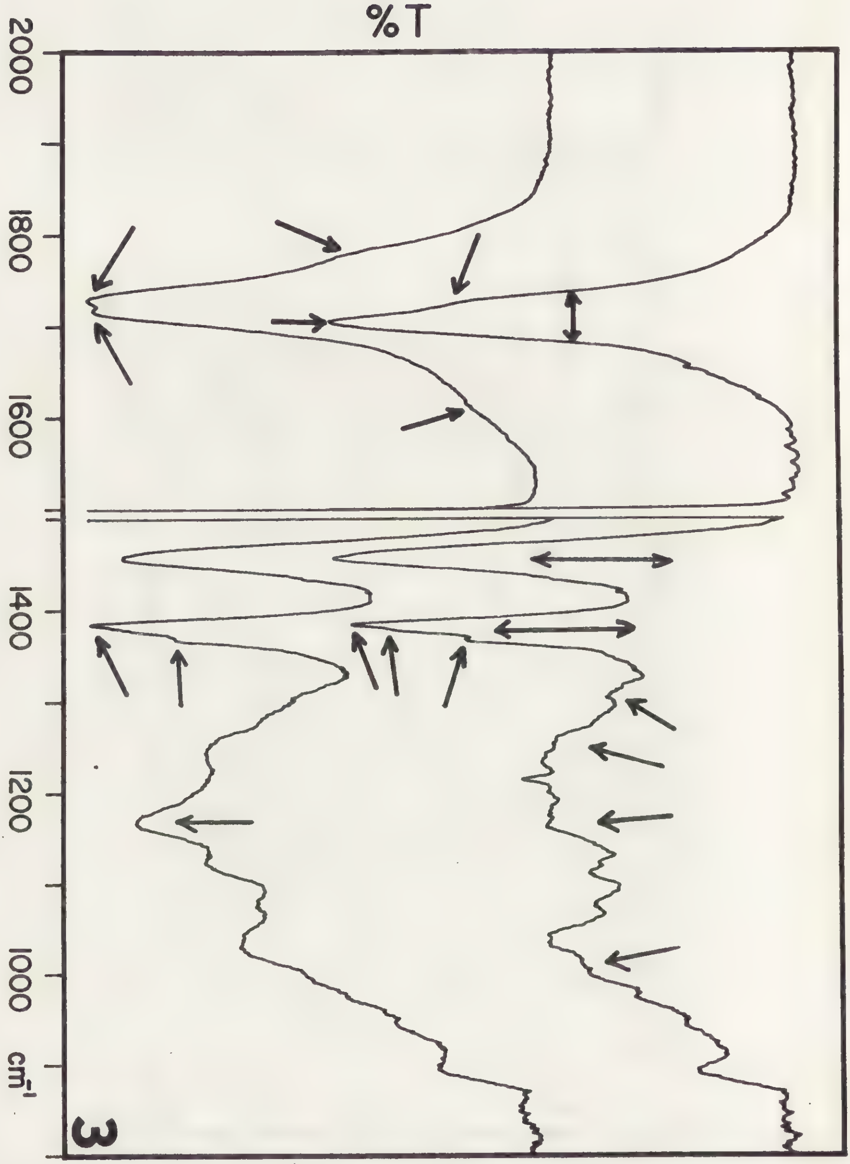
78/16/5/6



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PECULARITIES OF GILDING AND SURFACIAL TREATMENT OF RUSSIAN ICONOSTASES CARVING OF THE XVIIITH CENTURY

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PECULIARITIES OF GILDING AND SURFACIAL TREATMENT OF RUSSIAN ICONOSTASES CARVING OF THE XVIIITH CENTURY

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The most prominent achievement of Russian art of interieur ornamentation of second half- last XVIII century manifested in a number of gilded carved iconostases. Iconostasis of that time was a festive and magnificent receptacle of icons. Its architecture became more plastic and characterized with splendor of gilt and silvering on plane, convex and concave surfaces that emphasized special and compositional effects. High through carving framing cells for icons is combined with low relief of stucco moulding and gesso carving on backgrounds. Polychromy of round sculpture is combined with various textures of gilded surfaces that gave utmost possibility to use advantages of materials. Areas and coloristic features of icons that were executed by means of varnishes, dark grounds and underpaintings were constructed considering such surroundings. In icon painting it is widely spread effects which you cannot meet in secular painting of that time, leaf and burned gold and silver being covered with colored varnishes modifying extent and hue of their glitter.

One of the best iconostases is the iconostasis of the Assumption Cathedral in Velikiy Ustyug 1781-

1786 created in the Russian Classicism style. Architecturally the iconostasis divides into two tiers. The lower one with local icons decorated with a portico of flute columns with Corynth capitals interwined with flower garlands and ironed with strongly protruded frieze and cornice. The cornice has a shield with Holidays scenes. The second is the Apostolic tier with the Passion over it. The carved crucifiction with saints fixed above is integrate with iconostasis architecture by two huge carved volutes. Details of floral ornament with elements of Rococo are carefully elaborated. Good preservation of finishing enables to appreciate textural and coloristic diversity created by gilders. Yellow gilding is prevailing but some details have green gilding. Icon cases built up along the walls and around Western pillars were gilded with double gilt simultaneously with the iconostasis. Lustrous gilding combines with a mat one on the flat details. and on those having incisions and notches. Separate details: veins, cavities in flowers and leaves, flutes of columns are covered with reddish golden varnishing. Strokes of brushes by which the varnishing has been applied are visible. Making gradation of light refraction much more complex varnishing heightens its relief and increases color and tonal diversity of gilding

hues strengthens general effect of the whole ensemble.

The history of creation and further existence of the monument is reflected in documents that are stored in the State Vologda Region Archive in Velikiy Ustyug. It is possible to compare actual data with archival ones since it is known that this iconostasis has never been regilded. Account-books of the Cathedral and contracts signed by executors contain information about craftsmen, materials, technique and technology, dates and organization of work. The Velikiy Ustyug Cathedral which was in that time an eparchial city has to be "a model for all others" and for its decoration the State provided some means. Craftsmen were invited from different towns and regions. Modeller, carver and gilder were from Moscow. The contract signed by the gilder "the coachman of Moscow-Pereyaslav Yamskaya Sloboda Peter Alixandrov of Labzin". An obligation to produce the drawing of each detail before it was made proves qualification of the masters. Sculptures for the iconostasis were made upon drawings by Labzin in Yaroslavl, Labzin made also signed standards of his works ("trial pieces signed by my hand"). Already being assembled the iconostasis had to be dismantled for gilding. Work was done in specially adjusted premises. Some cellar fitted out to solve gold and even

in summer to prepare and store gesso and poliment. Special attention was paid to prepare ground for gilding and to surface finishing. The quality of gold, gilding of carving and sculpture with yellow gold on poliment (red gold) and with green-gold when "this would be ordered by decency" were specified as well as the areas which was to be mat, or those to be of"pure lustre" or gilded in parts and covered in its shades with the best varnish.

Varnishing of iconostasis carving of Velikiy Ustyug the Assumption Cathedral was examined by experts of the Department of Physico-Chemical and Mechanical Examination in the Institute of "Special Designing Restoration (Spetsproektrestavratsiya). of the firm "Rosrestavratsiya" ("Russian Restoration"). It was examined by means of IR spectoscopy. The examination revealed that is contained oil of linseed kind and of amber. Analitically (by means of spot test) presence of oil and amber was proved. Varnish had no pigment. It is proved also that varnishing was not continuous by partial.

Partial varnishing was widely used for additional optical and textural effects in dedorative art of the second half of XVIII - early XIX centuries. Thus the iconostasis of the Assumption Cathedral in Dmitrov 1690 (it was newly gilded in 1805)deepened

details of carving were covered with matting composition that hightened details being gilded and varnished.

It is necessary to examine and preserve varnishing an important component of artistical appearance of the interieur of churches and palaces. During restoration it is possible neither regilding nor any other treatment that will be able to alterate surfaces finishings already suffered through time effect.

USE OF POLYETHYLENE AS A PROTECTIVE COATING

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USE OF POLYETHYLENE AS A PROTECTIVE COATING

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Standard principles to be observed in the choice of preservation material are that the selected material shall not affect adversely the normal processes of degradation of the document, that it shall not enter into chemical reaction with the document components and that, by its composition and appearance, it shall be as similar as possible to the material of the document itself.

In introducing synthetic polymers to preservation practice, these principles must be treated in a more flexible way since there is no synthetic polymer that is similar to the material of the document neither by its appearance nor by its composition. On the other hand, many synthetic polymers provide a possibility of preservation of documents in cases where, with standard materials and methods, it was impossible.

At the selection of synthetic materials, we should be rigorous with chemical analysis of the materials because we must rely on exact analysis as a criterion of evaluation. We have only limited practical experience about properties and durability of synthetic polymers. Each selection of the preservation material therefore should be accompanied by a thorough analysis of the properties, kinetics of degradation processes and products resulting from these processes. All tests should be performed in such a way that the tested material is being examined as a part of the polymer-document system.

When such a system is exposed to any outside influence, chemical processes are initiated and their development importantly influences the further integrity of the document. Introduction of the new material into the system in a preservation undertaking inevitably effects the condition of the original material either beneficially or adversely.

What gives a preservation undertaking a special status is the fact that such undertaking cannot be repeated; it can only be poorly simulated since we have not an identical object for experimentation. In order to obtain desired results with the preservation undertaking, the material which is being brought into the system

should be chemically compatible with all components of the system and the same must hold for the products of spontaneous degradation processes of the material. Consequently, in addition to the knowledge of physical and chemical properties of both - the object and the material which is to be used for preservation - we should also know something about the kinetics and the products of possible processes of degradation.

One of especially interesting preservation materials is polyethylene, announced by Wilson and Forshee in 1959 /1/ as a promising material which should be examined.

By its chemical structure, polyethylene is polyolefin, a relatively inert and stable polymer having its structure as per infra-red spectroscopy:

$$H_3C - (CH_2\text{-}CH_2)_m - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}} - (CH_2\text{-}CH_2)_n - \underset{\underset{\displaystyle O}{||}}{C} - (CH_2\text{-}CH_2)_p - CH_3$$

The oxygen in this chain is an unitentional impurity. The polymer structure and properties are closely connected with the method of polymerization. Consequently, there are three types of polyethylene based on the polymerization type. Properties and differences between these three are shown in the Table I.

TABLE I

Parameters	Type of Polymers		
	High Pressure	Low Pressure	Medium Pressure
Molecular Weight	1000-45000	70.-400.000	60.000-400.000
Density gr/cm^3	0.92-0.93	0.94-0.96	0.96-0.97
Degree of Crystal.	53-67	80-90	85-93
Number of Methyl groups per 1000 C-atoms	20-40	5-15	1.5-5.0
Number of double bindings per 1000 C-atoms	0.3-0.6	0.3-0.8	1.2-1.5
Melting temp. °C	108-110	120-134	127-130

High pressure polyethylene is characterized by a branched molecular structure due to which it has a lower degree of crystallinity and lower melting point in relation to the analogous polymers of more linear chain structure. Besides, on the tertiary C-atom, there is a greater possibility of oxidation at the branching points so that this type of polymer oxidizes more easily.

Polyethylene, as other polyolefins, is characterized by relative inertness, i.e., most reactions that can be observed occur only at higher temperatures so that during normal protection and handling of the document these reactions will develop very slowly if they occur at all.

Thermal degradation of polyethylene in the absence of air is most noticeable at temperatures of about 300°C /2/; its rapid oxidation with oxygen from air occurs at the temperatures close to the melting point. /2/

Besides the temperature, the speed of reaction development is also influenced by the polymer crystal structure so that the high pressure polyethylene with the lowest density and lowest degree of crystallinity is most reactive,which is obvious from the Table II.

TABLE II

Type of Chemical Reaction	Temperature °C	Activation Energy
Thermal degradation	295-305	36 Kcal/mol
	335-360	70 Kcal/mol
Oxidation with oxygen from air	150-160	28 Kcal/mol
	160-200	20.5 Kcal/mol

From the above Table it is obvious that all rapid reactions take place within the temperature ranges that are not characteristic for the document preservation conditions. The system document-polymer can find itself close to these temperatures only for a short time - during the process of preservation itself. That is why it is necessary to select the lowest possible temperature of application and to keep to the minimum the time during which the system is exposed to the severe conditions.

It is interesting to follow the oxidation reaction kinetics in relation to the polymer structure. Figure No. 1 shows the kinetic curve of polyethylene oxidation. It is obvious that the polymer crystal structure provides an obstacle for development of oxidation reactions so that, at the temperature lower than the melting point, the branched polymer oxidizes twice as fast as the linear chain type.

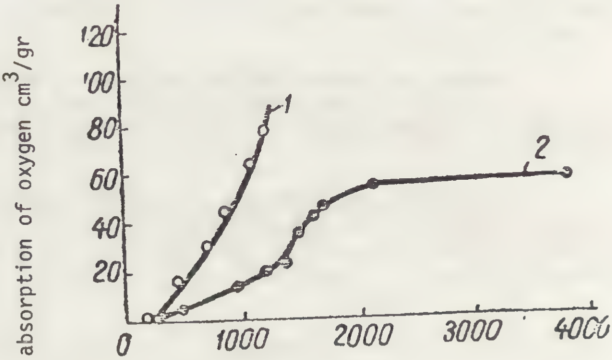


Figure No. 1

Kinetic curve of oxidation/ 0.92 gr/cm^3/ 1 and linear chain/0.958 gr/cm^3/ 2 polyethylene at 80°C

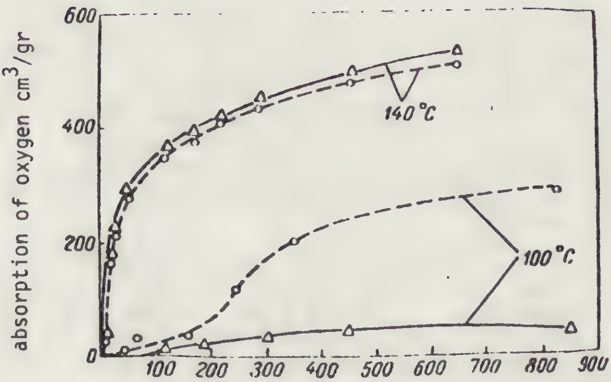
If the same reaction is observed at the temperature below and above the melting point, it is obvious that the polymer crystal structure is an obstacle for the oxidation reactions since, at temperatures above the melting point, the speed of reactions suddenly increases for both types of polymer.

Figure No. 2

Kinetic curve at temperatures above and below melting point

------ branched

——— linear chain polymer



Time in Hours

Polyethylene oxidation becomes measurable at 80°C, while photo-oxidation occurs under influence of UV-rays at the light absorption of 2900-3300 A wavelengths, the absorption range of carbonyllic groups. /3/

Generally, it can be taken that oxidation processes develop in two phases; in the first phase hydroperoxides are formed and in the second one these hydroperoxides are being decomposed and various products of decomposition are formed. The so formed free radicals often cause cross-linking.

Experience obtained in application of polyethylene in the preservation of documents is primarily connected with the preservation of new printed materials by lamination. When Forshee suggested that polyethylene would provide good possibilities for lamination of documents, it was a signal for further examination of this material.

Its good optical, mechanical and chemical properties have rendered it an interesting material for preservation of new printed matter on bad quality paper, damaged to such extent that its handling is impossible. But, in the application of lamination technique with thermoplastic foil one of the preservation postulates is not respected - that the material used should be similar to the material of

the document, and that it should not be visible - all thermoplastic foils are quite different from the paper cellulose and they are visible on the document.

That is why the lamination method of preservation should not be applied in the case of particularly rare and valuable documents. But it is useful in the preservation of materials from 19th and 20th century and older almost completely disintegrated materials.

In these cases, polyethylene provides very good possibilities since it has a very low melting point so that the application temperature is relatively low. Besides, duration of the document exposure to the temperature is very short so that it cannot greatly influence on the kinetics of degradation processes.

In the process of preservation by lamination, it is very important to obtain a strong binding with the paper surface to which it is applied. This is the case with polyethylene since the paper is a porous material that provides good adhesion by physical or mechanical binding. If we consider that polyethylene has been used for preservation of objects whose mechanical strength was so small that it was immeasurable, we did not even compare the influence of polyethylene on the increase of mechanical properties of the object since it is obvious.

Documents preserved by polyethylene lamination can be utilized. They are legible and their durability is rather extended. We are able to observe behaviour of documents preserved some twenty years ago - they have not changed and the results of artificial aging promise a long durability of documents preserved in such a way.

If we keep in mind that it takes hours for all polyethylene reactions to obtain measurable quantities of products and we know that during lamination both - the document and the film - are exposed to the temperature of about 120°C for 30 seconds, it is evident that there is no immediate danger of damage. Due to its chemical stability, polyethylene does not react with components of the object of preservation. The polyethylene film that is used is free from any additions.

The last requirement imposed to the preservation undertaking is reversibility - and it is known that polyethylene is not soluble in any solvent at the room temperature; it dissolves only at about 70°C.

Most preservation experts are concerned with this fact but, if we are realistic, there is practically no problem with removal of polyethylene. Actually, once dissolved and then cooled, the polymer does not make a film any more on the basis but it becomes white powder which is not transparent and which can be easily removed.

The penetration of polyethylene is not so deep and it can be completely extracted from the document. If decalin is used as an agent, working at 70°C is not unpleasant since there is no significant evaporation of decalin at this temperature and, in addition, it is not toxic.

For lamination of documents nowadays cellulose acetate is used as an alternative. Compared with polyethylene, we believe this thermoplastic film has lost the advantage, but with the synthesis of new materials polyethylene shall also be replaced in the future by an even better material.

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A RESIN FOR COATING TEMPERA PAINTINGS: ITS PHYSICAL AND CHEMICAL PROPERTIES

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A RESIN FOR COATING TEMPERA PAINTINGS: ITS PHYSICAL AND CHEMICAL PROPERTIES

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Creating polymer - based varnishes for paintings, particularly for tempera paintings, seems to be a burning problem. Materials now in use - such as and some resin and oil varnishes - turn yellow and crack long before the Life-time of a work of art itself is over. The composition of natural resins and drying oils is extremely complex and their oxydation and destruction practically cannot be controlled. As the result, the upper film layer turns first yellow, than black, becoming brittle and almost wholly insoluble.

In creating new polymer-based compositions we proceeded from the requirements that have already been mentioned in a number of papers:

1. The varnish must be transparent and colourless.
2. Its formulation should be known.
3. The resin must be elastic, but not tacky.
4. It should be soluble in organic solvents whose working properties make them suitable for coating paintings (toxicity, volatility).
5. The coating must be reversable, that is it must contstantly remain soluble (or swelling) in organic solvents.

The primary function of a varnish is protection against deterioration from:

a) dust and abrasives;
b) water steam, organic solvents and gases;
c) various kinds of radiation.

Most film-forming coating materials employed in

chemical industry cannot be used in the restoration of paintings for the following reasons: either the polymers used are thermo-setting, that is they tend to lose solubility (epoxide and polyester resins) or they have a too shiny cold lustre which makes them unsuitable for restoration purposes (acrylic resins).

As is known from the literature such synthetic resins as polyvinylacetate and polymers of methyl methacrylate and acrylate are now used as varnishes for paintings. We think, however, that their use is unjustifiable polyvinylacetate is not sufficiently weather-resistant and elastic, while polyalcylacrylates have the cold lustre which impedes the adequate perception of a work of art.

In our opinion, the synthetic resins that most approximate natural ones are alkyd resins. These are unsaturated polyesters modified by fatty oils - the basic ingredients of natural resins (drying oils). However, alkyd resins are not sufficiently weather-, moisture- and light-resistant, besides, their decorative properties tend to change in the course of time.

Recently in the USSR a number of improved (weather-resistant) alkyde resins have been created by copolymerising them with other polymers. In particular, the copolymerisation of alkyde resins with polyorganosilicoxanes endows the resulting materials with such valuable properties as high weather-, moisture- and heat-resistance, as well as resistance to various kinds of radiation.

In creating a new varnish due consideration should be given to the following two aspects:

1. It must fulfil all the requirements pointed out above;

2. Its initial properties should remain the same

as long as possible, that is, it must be ageing resistant.

Experimental work, therefore, was carried out in the following way. Each version of varnish was applied by a restorer to white and blue tempera samples; after the formation of a film the best versions were selected. The evaluation of varnishes was based on the following working and decorative properties: convinience of application, viscosity, toxicity and volatility of the solvent employed, film transperancy and absence of lustre.

Subsequently the selected versions were subjected to artificial ageing and compared to natural varnishes after which the final decision was made.

At first some weather-resistant thermoplastic film-forming materials were tested, such as the F-42 and F-43 "Ftorlons", the AR-528 and BMK-5 acryl resins and the AKO-45-80 and AKO-45-66 alkydosiloxane resins.

The experiments showed that the "Ftorlons" were not sufficiently adhesive, their solutions being highly viscons at minimum concentications and the solvents toxic. As regards the acryl resins they had an undesirable cold lustre.

A varnish based on the AKO (45-80 and 45-60) resins proved to be best of all, in respect to both its working and decorative properties. It is of moderate brilliance and has a warm tint which aclds to the integrity of a painting. The resin is soluble in such non-toxic solvents as pineue and white spirit. The working properties of the AKO resins are similar to those of natural resins: they are applied by brush or cloth pad and dry up at an appropriate and controllable rate to which restorers havegot used to. To encrease the rate of drying the resin may be dissolved in

sush readily-boiling solvents as petroleum ether (boiling point 40-70° or 75-100°) or ketones.

AKO resins are the result of the copolymerisation of alkyde resin with oligomer organosilicon compounds in the ration 2:1. PF-060, a pentaphthalic alkyd resin containing semi-drying soy-beau and sunflower-seed oil, as well as pentaerythritol and phthalic anhydride is used as a starting substance, while the FES-60 and FES-80 oligomer organosilicon compounds of polyhenylethoxysilicone (molecular weight 1580) serve as comonomers.

Films formed by AKO resins have valuable physical and chemical properties: their hygroscopicity and water absorption are, 1-2.5% and 4-6% respectively, that is much lesser than in the case of alkyde resins, while their mechanical properties are no less equal than those of films formed by natural resins, film hardness being 0.52-0.62 (as measured on the M-3 pendulum instrument), impact strength - 50 kg/cm (on the U-2 instrument), elasticity - 1 mm (on the MG scale).

Since the main function of varnish is, on the one hand, protection of paintings from various environmental effects and, on the other hand, retaining its properties for a long time, the entensity of ageing of the proposed version under the action of such agressive factors as light radiation and hish atmospheric humidity and temperature was studied in detail.

A seing effects were noted by yellowness of the upper film layer, loss of brilliance, as well as by a change in the mechanical properties of the varnish and its solubility in organic solvents.

At the first stage of the experiment the AKO resins were put under test along with all the natural resins currently used as coatings for paintings: dammar, shellac and acrylic mastic. Our aim was to compa-

re the intensity of the ageing processes in each instance.

As is known, the spectrum of the xenon lamp most approximates the daylight spectrum; the samples were subjected, therefore, to light ageing in type IPK-3 climatic champer with a xenon radiation source for 140 hours at a temperature of 40°C and humidity of 80%. The dagree of yellowness, cracking and cross-linkage served as a basis for a preliminary selection. The investigation showed that the varnishes based on natural resins reveal a distinct tendency to turn yellow and change their mechanical properties, in particular, dammar, mastic and shellac resins turned yellow and cracked, films of acryl mastic became intensively yellow and almost fluid, whereas the AKO films showed no visible changes.

At the later stages only the AKO resins were investigated, dammar and mastic resins being used as reference samples.

As is known, transparency and colourlessness of varnish films is characterized by the transmission coefficient in the visible spectrum region, transparency increasing directly with the coefficient value. A distinct result of varnish ageing is a change in its decorative properties: yellowness and loss of brilliance.

The transmission coefficient values for dammar and mastic resins and the AKO resins were obtained before and after ageing. For that purpose varnish samples were applied upon quartz glass plates and dried up in a heat chamber at 40°C. The transmission coefficient values were metered on type SFD-2 spectrophotometer in the spectrum region of 400-1000 mm. In their original state all the varnishes were transparent, the

transmission coefficient value being 100%. However, after ageing their decorative properties varied differently: the transpareny of the AKO resin remained almost the same (96%), while the transmission coefficient values of dammar and mastic resins fell to 75% and 60% respectively.

Tempera samples coated with different varnishes were tested on brilliance loss both in a climatic chamber and in the natural environment. The degree of brilliance was measured on type FB-2 photometer. The photoelectric method consists in evaluating the photocurrent induced in a photoreciever by a pencil of light reflected by a coating surface. The values obtained before and after ageing were plotted and variations in brilliance loss (BL) were determined. The brilliance loss in the natural resins (90%) was almost twice as much as in the AKO resin (55%).

The varnish samples were also subjected to ageing at a temperature of 60°C and humidity of 100% in type G-4 hydrostate for 10 days. The experiment revealed that type of ageing did not affect the decorative properties of the AKO resin, whereas dammar and mastic films beçame whitish and wrinkled and their hydroscopicity increased.

The change in the decorative and mechanical properties of varnish films was a result of various reactions in polymer molecules caused by ageing. Qualitative and quanditative changes in the molecular structure at the atom group level may be detected by infrared spectroscopy; the more pronounced are the changes the more intensive is the ageing process.

Infra-red spectral characteristics were obtained for AKO, dammar and mastic films before and after ageing. As it is impossible to have free films from natu-

ral varnishes they were produced on CBR crystals. The spectra were registered on type I-20 IR-spectrometer. In the AKO IR-spectra minimum variations were observed an indication that almost no reactions occured in the polymer moleculas. In the dammar and mastic IR-spectra substantial changes could be seen in the region of 1725 cm^{-1}, which corresponded to an increase of amount of carbonyl groups indicating to a cross-linkage process. Spectral peaks in the region of 3280-3520 cm^{-1} indicated than an amount of carboxyle groups in moleculas increased and oxydation took place.

That AKO varnish had been almost completely unaffected by ageing was confirmed by the fact that it retained solubility in such organic solvents as while spirit, xylole, etc.

As was peinted out above, the primary function of varnish is protection of paintings against variaus kinds of dangerous radiation, steams and gases.

The radiation which one encounters most frequently is ultra-violet radiation. So, to find out how AKO varnish fulfils its protective function its transition coefficient was evaluated in the ultra-violet region (250-400 mm). The experiment showed that the transition coefficient value of AKO films was lesser than it was in the case of natural varnishes. In other words, AKO-based varnishes, being transparent in the visible spectrum region, protect paintings from ultra-violet rays better than natural varnishes.

The degree of protection from steams and gases is characterized by the reciprocal of the steam permeability value. Steam permeability defined as the amount of water (mg) lost by 1 square centimetre of film surface was evaluated. The result revealed that the steam permeability of natural varnishes is almost twice as

great as the steam permeability of AKO varnish; in other words, synthetic varnishes are by no means inferiour - and often superiour - to natural varnishes, as regards the protection of paintings from steams and gases.

In summary it may be said that AKO resin as a varnish for tempera paintings is not only quite suitable by its decorative and working properties, but, what is more important, is far more weather-, moisture - and light resistant than natural varnishes. Resistance to ageing is a great advantage of the resin as it enables to prolong the intervals between restorations thus minimizing their traumatic effect upon a work of art.

APPLICATION DES TECHNIQUES NUCLEAIRES A LA CONSERVATION

Coordinator : Chr. de Tassigny (France)
Assistant coordinator: R. Ramière (France)
Members : S. Delbourgo (France)
G. Delcroix (France)
F. Flieder (France)
P. Mitanov (Bulgaria)
M. Stefanaggi (France)
J. Taralon (France)

Programme 1975-1978

1. a) Recensement des problèmes liés à l'altération des bois polychromes et collecte d'échantillons polychromés anciens dans les musées;
   b) étude analytique des conclus polychromes avant et après impregnation par des monomères (Delbourgo).
2. Application des techniques d'irradiation gamma à la conservation d'objets ethnographiques: desinfection et consolidation (Delcroix).
3. Desinfection des cuirs et parchemins par irradiation gamma: étude biologique et étude de la résistance physicochimique des matériaux irradiés, avant et après vieillissement artificiel (Flieder).
4. Consolidation de bois polychromes: fabrication d'échantillons; étude du pouvoir solvant des monomères; étude des conditions de la polymérisation; choix d'une méthode pour des cas réels; étude de la compatibilité des polymères avec les matériaux constitutifs de la polychromie; nouvelles protections de la surface (Mitanov).
5. Etude des problèmes pratiques liés au traîtement de consolidation d'objets en pierre (méthode par irradiation gamma): nettoyage, possibilités de restauration (Ramière).
6. Etude de la morphologie des différents types d'altération des sculptures sur bois polychromes.

   Etude de l'action des différents traîtements de conservation en fonction des types ainsi définés sur des bois polychromes altérés.

   Continuation des essais sur éprouvettes avec de nouveaux monomères (Stefanaggi).
7. Continuation des essais comparatifs de consolidation de matériaux pierreux par impregnation et irradiation gamma (Taralon).

8. Application de l'irradiation gamma au traîtement des bois gorgés d'eau: automatisation de l'extraction de l'eau (de Tassigny).

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RADIOCHEMICAL CONSOLIDATION OF PREHISTORIC TERRA COTTA POTSHERDS

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5th Triennial Meeting
Zagreb, 1978

RADIOCHEMICAL CONSOLIDATION OF PREHISTORIC TERRA COTTA POTSHERDS

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Abstract. In this paper we present our results and observations on the treatment and the behavior of prehistoric terra cotta potsherds, consolidated by gamma rays polymerization of synthetic resins.

Results on aging of terra cotta potsherds in atmospheric conditions, for more than I5 months are also discussed.

Introduction.

The conservation of ancient terra cotta objects require appropriate improvement of their physical and chemical properties,so that to withstand stresses of various origin,without important alterations or distortions .

With these requirements it is almost impossible to find methods which improve material without alterations . Improvement by itself means changes in the ancient material and due to this fact a compromise must be reached .

In this paper we report our results on prehistoric terra cotta potsherds,treated by styrene-polyester resin and polymerized by radiochemical method . The technique has been described elsewhere (I) . The radiochemical method seems to give acceptable results,although changes are inevitable from technological and archeological points of view .

Radiochemical Consolidation.

We have treated a small number of prehistoric potsherds,kindly offered to us by the National Museum of Athens,in order to study their behavior during and after consolidation . The potsherds have been cleaned with dilute hydrochloric acid,although a better technique is now applied in our laboratory (2),for dissolution of encrustations and other impurities,which close the pores of the material . Subsequently the potsherds were dried in an oven for several hours at IO5 ^{o}C .

After drying potsherds they were degasified under low pressure (about IO Torrs) in a vacuum chamber,in order to remove air and discharge pores . While the potsherds were under vacuum,a mixture of styrene-polyester (50:50%) was introduced into the chamber . After the potsherds were immersed into the mixture,a pressure of IO atm. was imposed with inert gas,in order to force the resin to enter as deep as possible into terra cottas . Nitrogen gas pressure was sufficiently high to ensure complete impregnation of the sherds . The potsherds thickness is between 5 to IO mm .

The impregnation process continues for about 24 hours, depending on the thickness of the sherds, their porosity etc. The potsherds were slowly depressurized in a period of 5 hours for reaching gradually to equilibrium . During this period a small amount of the mixture is going out from the sherds . In this way very clean sherds are obtained without secretion of liquid on their surface . The complete cycle of the treatment is depicted in Fig.I .

Irradiation by gamma rays is the next step of consolidation of the synthetic resin mixture into terra cotta . A dose of 4 to 5 MRads is given by our swimming pool reactor during shut down . The composite material obtained is very compact, having remarkable mechanical properties .

As shown in Table I the ages of the potsherds treated are 4000, I800 and I500 years B.C, and their origin is from Dimini, Aegina Island and Kakovato (see Fig.2).

Table I

	Origin	Age B.C	No Sam.	Color
D	Dimini	4000	IO	Brown
A	Aegina	I800	II	Green-yellow
K	Kakovato	I500	7	Dark

The weight before and after impregnation and irradiation for each sherd is given in Table II, as well as percent absorption of synthetic resin mixture . It seems that Dimini's potsherds are less porous than those of Aegina, and show the same average absorption characteristics of modern terra cotta objects (about I5%)(I) . Potsherds of Aegina and Kakovato have average percent absorption similar to that of Knossos (I) . The impregnation characteristics refer to the saturation of terra cotta by styrene-polyester mixture, under a pressure of IO atm.

A number of sherds from each batch was impregnated with distilled water under ambient temperature and pressure conditions, for a long period of time . The results

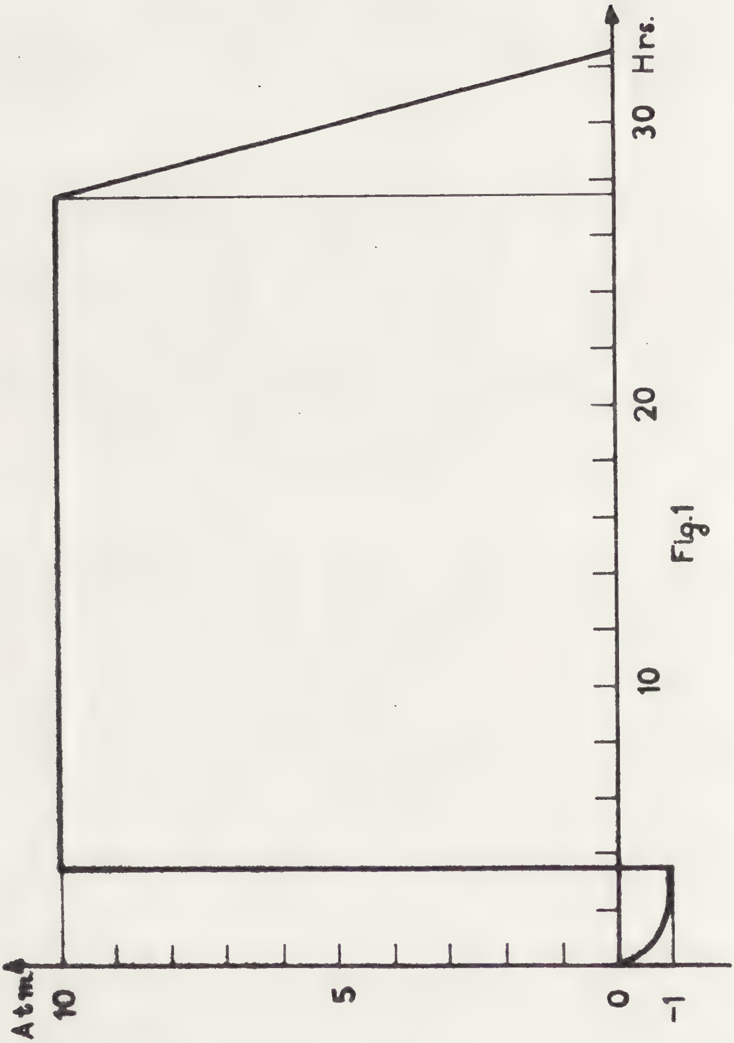

Fig.1

Fig.2

Table II
Impregnation Characteristics of Prehistoric
Terra Cotta Potsherds

Origin	Initial weight gr	Weight gr after impregn. gr	Absorbed s-p	Absorbed s-p %
ID	75,24	87,69	I2,45	I6,54
2D	57,99	67,I3	9,I4	I5,76
3D	54,73	65,95	II,22	20,05
4D	26,65	3I,42	4,77	I7,89
5D	24,74	28,I4	3,40	I3,74
6D	9,37	II,00	I,63	I7,39
7D	27,28	3I,22	3,94	I4,44
8D	25,I6	27,65	2,49	9,89
9D	20,00	22,48	2,48	I2,40
IOD	I6,95	I8,88	I,93	II,38
Mean values	33,8I	39,I6	5,35	I4,95
IA	50,38	64,II	I4,73	29,23
2A	33,82	4I,29	7,47	22,08
3A	3I,29	4I,I7	9,88	3I,57
4A	37,49	48,73	II,24	29,98
5A	36,47	47,05	I0,58	29,09
6A	30,28	38,46	8,I8	27,0I
7A	8,2I	I0,57	2,36	28,74
8A	I7,70	22,I0	4,40	24,85
9A	I9,23	25,79	6,56	34,II
I0A	I3,73	I6,85	3,I2	22,72
IIA	I0,40	I3,72	3,32	3I,92
Mean values	26,27	33,62	7,44	28,30
IK	2I,92	26,58	4,66	2I,25
2K	I8,98	22,29	3,3I	I7,43
3K	I5,85	I9,52	3,67	23,I5
4K	9,66	II,74	2,08	2I,53
5K	8,26	9,96	I,70	20,58
6K	9,6I	II,83	2,22	23,I0
7K	I6,35	I9,96	3,6I	22,07
Mean values	I4,37	I7,4I	3,04	2I,30

are shown in Table III in comparison with those of untreated potsherds .

Table III

Impregnation	Saturation absorption % D	A	K	Impregnation time h
Distilled water (before impregnation by s-p)	22,6	25,5		I45
Styrene-polyester (s-p)	I5	28,3	2I,3	24
Distilled water (after consol.)	I,9	I,8	3,2	800

The composite material obtained after consolidation is more compact,less porous and harder than terra cotta. It is chemically inert and seems to have a better mechanical strength than terra cotta . When exposed to atmospheric conditions no changes have been observed in a period more than I5 months .

Aesthetic Alterations.

The appearance of the potsherds after consolidation was slightly darker than before . The absence of synthetic resin desorption on the surface of the potsherds was surprisingly good . According to our opinion none potsherd has suffered alterations or changes of appearance which may be characterized as aesthetically unacceptable. A good deal of potsherds were painted on their external surface . However,no dissolution of the paint has been observed .

After immersion into distilled water for about 800 hours,no damage,alteration or distortion have been observed,and water absorption was very small (see Table III).

Drying of the sherds is short, showing that water is absorbed by a thin layer on the surface of the material . Indeed about 50% of the absorbed water was lost within 24 hours under ambient conditions . Crystallization of salts on the surface of the sherds has not been observed.

A number of potsherds has been exposed to UV radiation (UV lamp of 300 W) for about 300 hours, but no apparent damage or color alteration has been observed .

Exposure of a number of potsherds to atmospheric conditions for more than I5 months show good behavior , although color tends to acquire its initial earthy appearance . All terra cotta sherds show excellent compatibility with polyester-styrene polymer . In Fig.3 two pieces of terra cotta sherds from Dimini are compared, one exposed (right) to atmospheric conditions and the other (left) not exposed after consolidation .

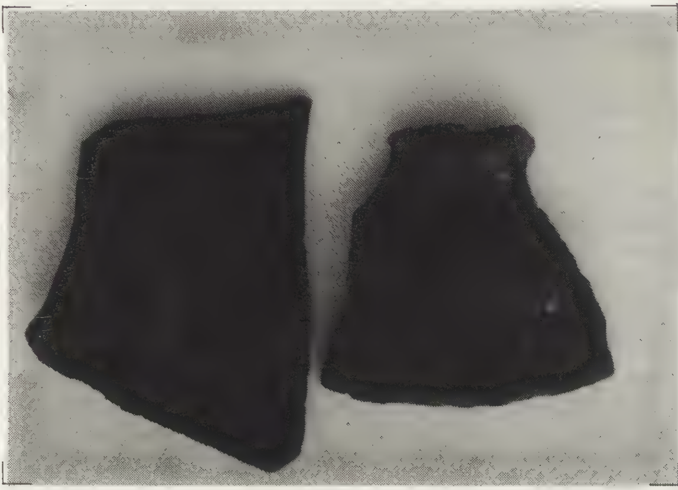

Fig.3

Concluding Remarks.

Radiochemical consolidation of prehistoric terra cotta potsherds with styrene-polyester mixture, seems to give satisfactory results and dangerous properties have not been observed at all .

Major aesthetic alterations or distortions are not observed even if subjected to severe aging conditions .

Although the aging of the materials obtained by radiochemical consolidation is not sufficiently long,we may conclude that the composite material resulting after consolidation shows remarkable properties .

Unfortunately it is impossible to test a great number of prehistoric terra cotta potsherds,due to their scarcity, in order to draw out better statistical conclusions . However,our program on the consolidation of terra cottas continues with other monomers or mixtures of them,like vinyl acetate,methyl methacrylate etc.

Acknoledgments : The author is indebted to Dr N.Gialouris,Director of the National Museum of Athens,Dr J.Sakelarakis,Head of the Prehistoric Collection of the National Museum of Athens ,the author also thanks Mr A.Antonopoulos and A.Kokkinos for their assistance .

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THE CONSERVATION OF ANCIENT BONES BY RADIOCHEMICAL CONSOLIDATION

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THE CONSERVATION OF ANCIENT BONES BY RADIOCHEMICAL CONSOLIDATION

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Abstract: In this paper we report our results on the consolidation of ancient human and animal bones, by the radiochemical method.

The combination of bones with vinyl acetate or methyl methacrylate seems to considerably inprove the strength of bones, even if they are in advanced deterioration, without major changes of their appearance. Alterations or distortions have not be observed after the treatment.

Introduction.

Nuclear methods have been applied for conservation purposes in many fields of archeology during the last decade. These methods have been applied with two general objectives:

a. Consolidation of materials and

b. sterilization.

Regarding consolidation, several porous materials have been treated like dry wood,waterlogged wood, stones and terra cottas[1][2][3].
Our purpose in this work is to present results on the consolidation of bones. Bones are of considerable archeological value requiring conservation frequently.
For the treatment of bones we have applied the same technique which has been developed in our Laboratory, for the consolidation of other materials like drv and waterlogged wood, stones,marble, terra cottas, etc., and described alsewhere[2][4].

The porosity of bones and its distribution.

Bones are composed of mineral salts (65-70%), deposited among a network of organic fibers (30-35%),which form a rocklike solid material. The internal structure of this solid is appropriate for accomodation of stresses, applied upon them during the life time of the organism. Most parts of bones have a spongy structure with a thin fibrous layer of compact bone (endosteum and periosteum) covering the osteoblast system, which is composed of narrow channels along the bone, called harvesian canals. Harvesian canals are surrounded by harvesian lamellae. Numerous small spaces or lacunae are found between them, each reaching the other by minute canals or canaliculi.
The entire structure of bones is, therefore ,pierced throughout by an extremely fine network of canals(like other porous materials).
Differences however exist between bones and other porous materials as stones and terra cottas. In the last materials the distribution of cavities is completely disordered when compared to the organized one of bones.
The spongy parts of bones can therefore easily be filled with the impregnation liquids, like synthetic resins. Due to the macroporosity

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Fig.I

of the structure, limitations arise. The retention of liquids is decreased when compared to microporous materials.

Treatment of bones.

We have treated a number of small pieces of human bones, originating from an ancient cemetery of minoan era (2400-1200 B.C), discovered recently by Dr J.Sakelarakis of the National Museum of Athens. The cemetery is found in Archanes (site Fourni), 5 kms on the south of Knossos, see Fig. 1.

All pieces of these bones are in relatively good condition, because site Fourni is a rocky hill with dry ground. The bones show a clear decay, they are fragile and their mechanical strength is reduced. In order to study the porosity of the bones for consolidation, we have treated a number of pieces. One batch was treated with vinyl acetate (VA) whereas one other with methyl methacrylate (MMA) as is shown in Table I.

Table I.

Batches of bone treated

Batch No	N° of pieces treated	Synthetic resin utilized
1st	8	VA
2nd	5	MMA

Both batches have previously been cleaned and subsequently impregnated according to our method. Nitrogen gas pressure has applied, in order to force liquid into small cavities. In this way bones compactness is improved.

Prepolymer-monomer mixtures have been used for impregnation, in a ratio 1:3, in order to obtain a less viscous and simultaneously penetrating liquid. Pressure is however needed, as mentioned before, if a good impregnation and higher retention is required.

//

Besides human bones, we have also treated an ancient animal bone which was seriously deteriorated.

Results and discussion.

The impregnation characteristics of the bones treated by synthetic resins is remarkable as shown in Table II. The absorption of resin corresponds to saturation conditions, under 10 atm pressure applied during impregnation.

The percent weight absorption and retention of synthetic resin has beenn calculated with the following formula.

$$\frac{B - A}{A} \cdot 100 = \left[\frac{C - A}{A} + \frac{B - C}{A}\right] \cdot 100$$

Where : A initial weight (before impregnation)
B weight after impregnation,
C weight after irradiation.

In the above formula the terms in the braket have the following meaning:

$\frac{B - C}{A} \cdot 100$ percent loss of the synthetic resin,

$\frac{C - A}{A} \cdot 100$ percent retention of the synthetic resin.

From the results of table II and above formulas, we find the mean values of table III for human bones.

We have performed a second impregnation for the animal bone, in order toachieve better retention and improve reinforcement of this friable bone. The results of the treatment are given in Table IV, while Fig. 2 shows bone appearance after consolidation.

Our samples have been irradiated in our swimming pool nuclear reactor, during shut down periods, with gamma ray doses given in Table II.

Loss of synthetic resin is observed after impregnation, as it is clear from Tables II and III. This is mainly due to the avaporation of monomer before and during irradiation (4). Resin post-irradiation loss (in the form of vapor) is also observed. It is probably due to non

Table II

Impregnation characteristics of human bones

Sample n°	Synthetic resin	Weight gr Initial	After Impregnation	After Iradiation	MRads
1	V.A.	2,80	3,99	3,20	2,2
2		6,75	8,91	7,72	
3		7,20	9,56	8,25	
4		6,86	10,12	7,87	2,9
5		9,88	13,10	11,00	
6		6,57	8,27	7,32	
7		8,29	11,77	9,40	
8		2,41	3,13	2,74	
Mean values		6,35	8,60	7,19	
9	MMA	13,43	18,03	14,61	2,9
10		6,63	9,26	7,35	
11		2,44	3,48	2,70	
12		1,53	1,99	1,67	
13		4,98	8,20	5,45	
Mean values		5,80	8,20	6,36	

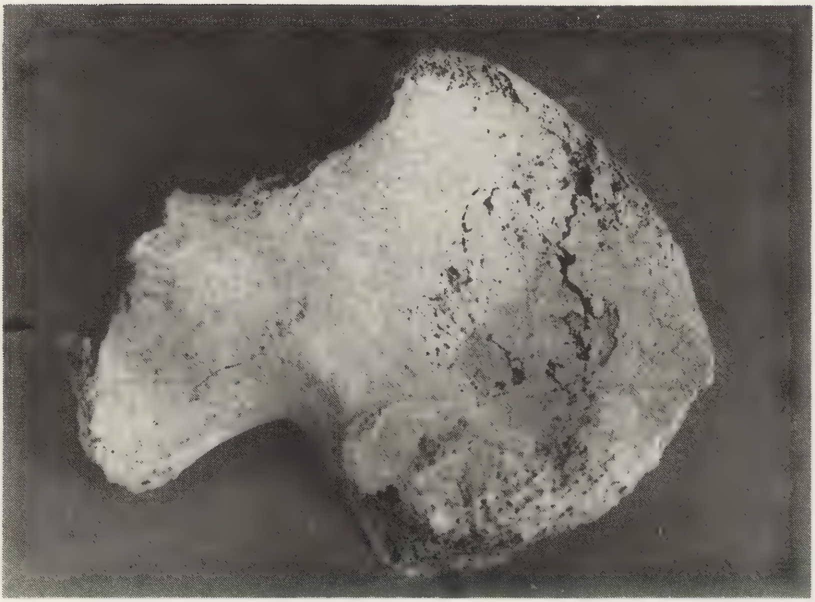

Fig. 2. Animal bone treated.

Table III

Percent loss and retention characteristics of human bones

	VA	MMA
$\frac{B-C}{A} \cdot 100$	22,2%	31,7%
$\frac{C-A}{A} \cdot 100$	13,2%	9,6%
$\frac{B-A}{A} \cdot 100$	35,4%	41,3%

Table IV

Impregnation characteristics of animal bone

Weight gr	Impregnation (VA)	
	1st	2nd
After impregnation	99,7	96,2
After irradiation	75,5	80,5
Final	74,2	79,4

Fig. 3. Human bones

polymerized monomer, especially of V.A. Smaller losses of MMA are observed.

No apparent differences have been observed between samples untreated and impregnated with VA and MMA. Untreated (Middle) and treated bone pieces with VA (left) and MMA (right) mixtures, are given for comparison in Fig.3.

The radiochemical method of conservation is worth considering since the appearance of bones remain the same and an improvement of their mechanical properties is obtained.

Acknowledgement. The author thanks Mr.Antonopoulos and Miss E.Kriara for their assistance.

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COMPATIBILITE ENTRE RESINES, CIRES ET POLYMERES, APPLIQUES DANS LA TECHNIQUE DE CONSERVATION ET DE RESTAURATION

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COMPATIBILITE ENTRE RESINES, CIRES ET POLYMERES, APPLIQUES DANS LA TECHNIQUE DE CONSERVATION ET DE RESTAURATION

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RESUME: Dans l'annonce on a traîté le problème de la qualité du film compatible et on a étudié la compatibilité dans un solvant d'après la méthode viscosimétrique et d'après une confirmation par IR spectroscopie de toute une série de paires de résines et cires naturelles ainsi que de polymères et cires synthétiques. Dans 6 figures (sujétions graphiques) on présente la sujetion viscosité spécifique-concentration des dissolvants; dans 11 sujétions graphiques est présentée la compatibilité des solvants des paires polymères et cires à différents rapports volumétriques des composantes à une concentration égale dans le même dissolvant. Dans 3 figures on présente les spectres IR imposés des substances pures et de leurs mélanges.

A la suite des recherches faites il est constaté que les paires "Cosmolloid 80 H/Acryloid B 72; Cosmolloid 80 H/copolymère d'acrylate de radiation -γ; Acryloid B 72/ Vinavil K 50; dammar/AW-2; Acryloid B 72/dammar; dammar/ copolymère d'acrylate de radiation -γ ont une bonne compatibilité à tous rapports. Les paires Acryloid B 72/cire d'abeille; dammar/mastic; gélatine/methylcellulose Celacol M 20 ont une compatibilité restreinte(seulement dansdes rapports déterminés des composantes). Les paires dammar/ cire d'abeille; gélatine/alcool polyvinilique Mowiol 50-98 sont incompatibles.

INTRODUCTION: L'application favorable de résines, cires et polymères dans la conservation et la restauration des valeurs culturelles contraint toujours à chercher des moyens pour améliorer leurs qualités physico-mécaniques et technologiques, à modifier leurs propriétés, dans le but de répondre aux exigences augmentées de la pratique de restauration. L'une des méthodes d'obtention des matériaux de polymères à propriétés nouvelles c'est leur compatibilité. Sous compatibilité de deux polymères on comprend leur capacité de former un système d'une résistance termodynamique homogène et monophase. On connaît toute une série de méthodes

pour apprécier la compatibilité: détermination de l'effet termique lors de la dissolution réciproque de 2 polymères (1,2,3), par mesurage de l'intensité d'absorbtion des groupes polaires dans un spectre infrarouge (4), méthode dilatométrique de transformation des mélanges de polymères en une masse de verre (5), analyse optique d'un film obtenu de mélange des polymères dissous (2,6), appréciation de la compatibilité par un degré équilibreur de dilatation du film compatible (7) et autres. La compatibilité des polymères peut être analysée non seulement à l'état solide mais aussi dans une solution (8). Le mesurage de la viscosité spécifique du système est un cas particulier d'analyse de la compatibilité dans une dissolution indépendamment du rapport des composantes. Lors de la détermination de la viscosité spécifique du système il est nécessaire de faire des mesurages dans un régime Newton du courant (2). Cela se réalise en faisant les essais à des tensions et vitesses de déplacement minimes. Lors de la détermination de la compatibilité d'après la méthode viscosimétrique il faut tout d'abord déterminer la viscosité spécifique des dissolutions des différents polymères et construire la sujétion graphique - viscosité spécifique/rapports volumétriques des dissolutions initiales. On construit la courbe additive (rectiligne) qui exprime les propriétés du système où les polymères n'entrent pas en actions réciproques. La sujétion graphique obtenue expérimentalement est au-dessus de la courbe additive lorqu'il y a une bonne solubilité réciproque des polymères et plus le degrés de compatibilité est meilleur plus la déviation augmente. Il y aura une compatibilité des polymères seulement dans le cas où la force d'action réciproque parmi les macromolécules des différents polymères est plus grande que l'action réciproque parmi les macromolécules d'un seul polymère. C'est alors que la viscosité du système augmente par rapport à la viscosité des différents polymères qui n'entrent pas en actions réciproques. On détermine la viscosité spécifique en se servant d'appareils standards pour l'étude de la viscosité des solutions polymères et par elle on porte un jugement sur la compatibilité entre eux. Les solutions possèdent une concentration égale dans des rapports volumétriques différents dans un même dissolvant.

Dans ce traîté on a mis à l'étude la compatibilité d'après la méthode viscosimétrique dans une solution de toute une série de paires de résines et cires naturelles et de polymères et cires synthétiques, sans prétention d'avoir épuisé toutes les possibilités concernant la pratique de conservation, à savoir: Cosmolloid 80 H/Acryloid B 72 - paire, utilisée pour la consolidation et en tant que couche protectrice des oeuvres d'art en bois, métal, peintures, icônes etc (9); Cosmolloid 80 H/ polymère de radiation, dammar/polymère de radiation, en rapport avec l'activité complexe de consolidation préalable, consolidation par imbibition de monomères et polymérisation de radiation subséquente et une couche protectrice définitive des icônes

et polychromie (10); Acryloid B 72/Vinavil K 50 - mélange pour la consolidation d'une couche protectrice des objets en métal; dammar/cire d'abeille, pour la consolidation de la première couche de peinture, couche picturale, moelle d'un arbre (10,11) et des polymères adhésifs comme suppléments(12); dammar/AW-2, paire expérimentale où l'on introduit la cire cyclohexanone qui par ses propriétés s'approche des couches de protection au vernis naturelles des icônes et peintures; Acryloid B 72/cire d'abeille en tant que composition de consolidation; dammar/mastic; Acryloid B 72/dammar, combinaison pour consolidation et couche de protection; gélatine/méthylcellulose, gélatine/alcool polyvinilique, combinaisons expérimentales dans le but d'introduire de nouvelles substances (polymères) en tant que composantes lors du collage de stabilité de la couche picturale pour des icônes et fresques.

MATERIAUX: Dammar, mastic, gélatine, cire d'abeille, produits des ateliers de restauration, Acryloid B 72(Rhom and Haas Co., phil., USA), polymère de radiation - bloc copolymère de butylméthacrylate et méthacrylate dans un taux de volume 3:1, obtenu par nous lors de l'irradiation à rayons -γ , à une température - 18°C, à la puissance de la dose 0,025 Mrad/heure, Vinavil K 50 (Montecatini, Italy), alcool polyvinilique Mowiol 50-98 (Hoechst), cire polycyclohexanone AW-2 (BASF), cire microcristalline Cosmolloid 80 H(Astor Boisselier and Lawr), méthylcellulose Celacol M 20 (British Celanese Ltd).

METHODE: Préparation des solutions initiales - on prépare des solutions d'une concentration 1g/100ml des polymères, cires et résines comme suit: Cosmolloid 80 H, Acryloid B 72, Vinavil K 50, polymère de radiation et cire d'abeille dans de toluène; dammar, AW-2, mastic et cire d'abeille dans de xylène , Mowiol 50-98 et gélatine dans de l'eau, Acryloid B 72,dammar et polymère de radiation dans dichloréthane. Pour la gélatine et méthyl-cellulose on a préparé des solutions initiales avec concentrations 0,1g /100 ml dans de l'eau. En ajoutant un dissolvant pur on prépare des solutions à la concentration 0.1, 0.2, 0.3,.....0.9g/100 ml et pour gélatine et méthyl-cellulose respectivement 0.01, 0.02......0.09g/100 ml.

La détermination de la viscosité spécifique par le viscosimètre de Pinkevich se réduit au mesurage des temps d'écoulement des quantités de volume égal de la solution et du dissolvant par la tube capillaire d'un diamètre de 0,6 mm. On fait 5 mesurages pour chaque concentration, en prenant la valeur moyenne. La viscosité spécifique se calcule $\eta_{sp.} = \eta$relatif -1, où:

$\eta_{rel.} = \frac{\tau}{\tau_0}$ τ - le temps de l'écoulement de la solution en sec. τ_0 - le temps de l'écoulement du solvant en secondes.

Les sujétions de $\eta_{sp.}$ de la concentration des solutions sont présentées dans les Fig. 1 à 6.

ETUDE VISCOSIMETRIQUE DE LA COMPATIBILITE DES SOLUTIONS DES POLYMERES, RESINES ET CIRES. Les données pour la con-

struction de la courbe additive sont obtenues en additionnant les viscosités spécifiques des solutions pures d'une telle manière que les concentrations soient complétées jusqu'à 1g/100 ml dissolvant. Par exemple la paire Cosmoloid 80 H/Acryloid B 72

$\eta_{sp.}$adit. I= $\eta_{sp.}$0.9% Cosmolloid 80 H + $\eta_{sp.}$0.1% Acryloid B 72

$\eta_{sp.}$adit.II= $\eta_{sp.}$0.8% Cosmolloid 80 H + $\eta_{sp.}$0.2% Acryloid B 72 etc. Pour la construction de la courbe expérimentale on commence par des solutions compatibles des deux composantes, obtenues par le mélange des solutions initiales avec la concentration 1g/100 ml à de différents taux. Après la constatation d'un équilibre termodinamique (24 heures) on mesure les viscosités des solutions compatibles - $\eta_{sp.}$.
DISCUSSION DES RESULTATS: Pour la paire Cosmolloid 80 H/ Acryloid B 72 la courbe expérimentale est au-dessus de la courbe additive c.à d. les polymères sont compatibles dans tous les rapports. Un pic fort de compatibilité existe dans le taux des composantes 7:3 (figure 7). Cosmolloid 80 H/ polymère de radiation sont compatibles dans toutes les compositions (fig. 8). De fig. 9 il est évident qu'Acryloid B 72 et Vinavil K 50 sont compatibles dans toutes les compositions. Dans la paire Acryloid B 72/cire d'abeille la courbe expérimentale croise la courbe additive. Dans une composition Acryloid B 72/cire d'abeille de 1:9 jusqu'à 5:5 le système est compatible et de 5:5 jusqu'à 1:9 il est incompatible (fig. 10). Dans dammar et AW-2 il existe une compatibilité dans tous les rapports des composantes. Il existe deux pics forts exprimés dans le rapport dammar/AW-2 9:1 et 4:6 (fig. 11). Dans polymère de radiation et dammar il existe une compatibilité dans tous les rapports (fig. 12), cela s'agit également pour la paire Acryloid B 72/dammar (fig. 13). Lorsqu'il y a une compatibilité de dammar et cire d'abeille la courbe expérimentale est audessous de la courbe additive, c.à d. il existe une incompatibilité dans tous les rapports des composantes - fig.14 c.à d. on obtient dans la pratique un mélange mécanique, tandis que pour mastic et dammar la courbe expérimentale croise la courbe additive, c.à d.les résines ont une compatibilité restreinte, elles sont compatibles dans des rapports mastic/dammar 8:2 et 9:1 et incompatibles de 8:2 jusqu'à 1:9 (fig. 15). La gélatine et la méthyl-cellulose sont compatibles dans un taux de 9:1 jusqu'à 6,5:3,5 et dans un taux de 6,5:3,5 jusqu'à 1:9 elles sont incompatibles (fig. 16). Lorsqu'il y a une compatibilité de gélatine et Mowiol 50-98 la courbe expérimentale est au-dessous de la courbe additive, c.à d. dans tous les rapports des composantes le mélange est incompatible (fig. 17).

Parallèlement aux études de la compatibilité d'après la méthode viscosimétrique nous avons vérifié l'application de la spectroscopie infrarouge. Les spectres ont été photographiés sur un spectrophotomètre infrarouge UR-10 de la Maison "Carl Zeiss" dans sa zone medium (de 800 jusqu'à

3600 cm-1), qui est en relation avec les transitions vibratoires dans la molécule. Pour éliminer l'action du dissolvant et pour faciliter l'interprétation des résultats nous avons préparé les échantillons sur l'aspect d'un film. Dans ce but nous avons procédé à la dissolution de 40 mg polymère dans 1 ml dissolvant - gélatine et Mowiol dans de l'eau et les autres dans de toluène Les solutions d'eau et leurs mélanges (1:1) étaient versés sur des plaques de AgCl, et les autres dissolvants polymères et leurs mélanges - sur des plaques de KBr. Les taux de mélange étaient: Cosmolloid 80 H/Acryloid B 72 - 1:1, Acryloid B 72/dammar - 1:1; Acryloid B 72/cire d'abeille - 7:3, dammar/mastic - 1:9, cire d'abeille/dammar - 1:1. Nous avons choisi ces taux en raison directe de l'appréciation directe de la compatibilité d'après la méthode viscosimétrique. Lors de la comparaison des spectrogrammes des substances pures et de leur mélange dans la paire cire d'abeille/dammar (fig. 18) on n'a pas découvert des modifications dans les spectres des mélanges par rapport aux spectres des substances pures. Dans le spectre du mélange dammar-mastic, pris dans un taux 1:9 (fig. 19) on aperçoit une déviation vers des fréquences du pic du groupe carbonile plus basses (de 1720 à 1710 cm-1). On aperçoit des processus pareils et dans l'autre domaine d'absorbtion des groupes carboniles (1000-1400 cm-1). Probablement ces modifications sont dûes à la polarisation des groupes carboniles et leur participation dans la formation de liens de protons hors-moléculaires. Alors s'effectue une augmentation du moment bipolaire, accompagnée d'une diminution de la densité électronique. Donc, dans ce taux des composantes on peut considérer le mélange compatible. Dans le spectre du mélange Acryloid B 72/Cosmolloid 80 H - 1:1 (fig. 20) on aperçoit une modification dans le taux des pics à 2990 et 2960 cm-1, correspondant à l'absorbtion respectivement de CH_3- et CH_2-groupes de la chaîne d'Acryloid B 72. La modification s'exprime par l'augmentation de l'intensité du pic des groupes CH_3. Les raisons pour tout cela s'avèrent les déformations de valence des liens en conséquence des processus de polarisation arrivés et l'équilibre énergétique nouveau constaté parmi les molécules du mélange. Tous les résultats concurent bien avec ceux obtenus par une méthode viscosimétrique.

CONCLUSIONS: On a étudié la compatibilité dans une solution d'après la méthode viscosimétrique avec confirmation d'après la spectroscopie IR de toute une série de paires résines naturelles, polymères et cires. A la suite des études faites on a constaté que les paires: Cosmolloid 80 H/Acryloid B 72; Cosmolloid 80 H/polymère acrylate de radiation; Acryloid B 72/Vinavil K 50; dammar/AW-2; Acryloid B 72/dammar et dammar/polymère acrylate de radiation ont une bonne compatibilité. Acryloid B 72/cire d'abeille; dammar/mastic; gélatine/méthyl-cellulose ont une compatibilité restreinte et les paires dammar/cire d'abeille et gélatine/Mowiol 50-98 sont incompatibles.

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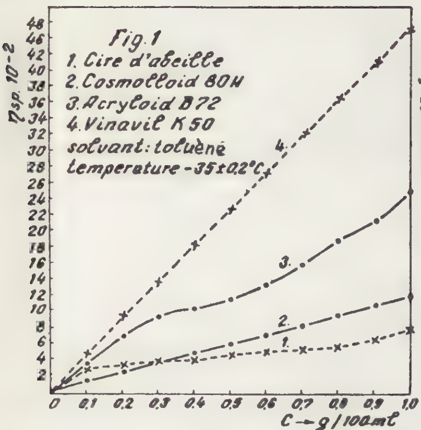


Fig. 1
1. Cire d'abeille
2. Cosmolloid 80H
3. Acryloid B72
4. Vinavil K 50
solvant: toluène
temperature - 35±0,2°C
ηsp. 10⁻²
C → g/100ml

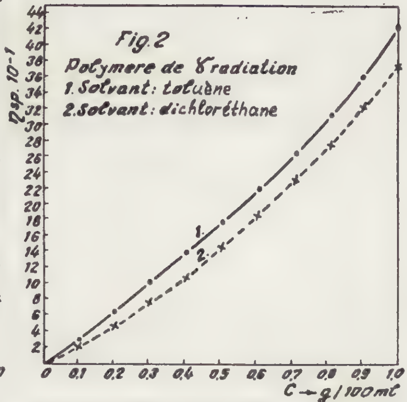


Fig. 2
Polymere de γ radiation
1. Solvant: toluène
2. Solvant: dichloréthane
ηsp. 10⁻¹
C → g/100ml

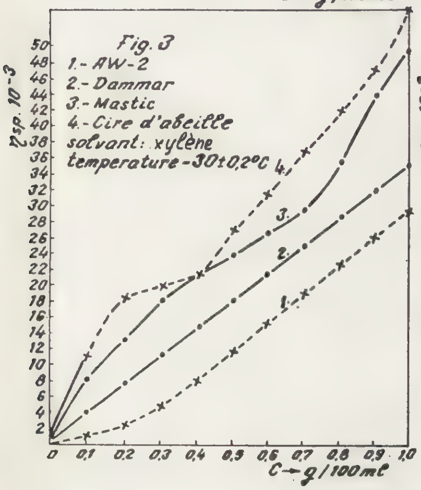


Fig. 3
1.- AW-2
2.- Dammar
3.- Mastic
4.- Cire d'abeille
solvant: xylène
temperature - 30±0,2°C
ηsp. 10⁻³
C → g/100ml

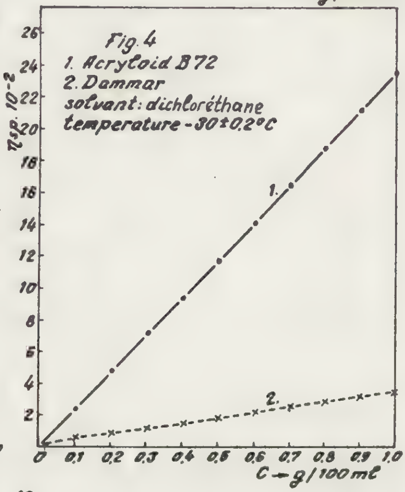


Fig. 4
1. Acryloid B72
2. Dammar
solvant: dichloréthane
temperature - 30±0,2°C
ηsp. 10⁻²
C → g/100ml

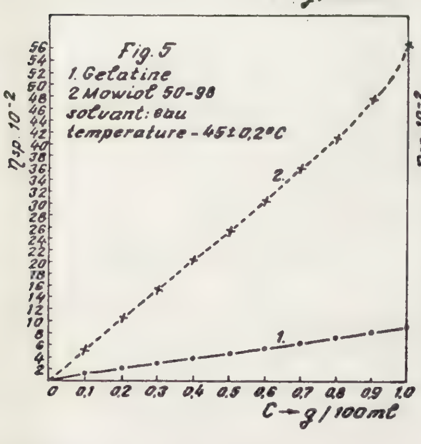


Fig. 5
1. Gelatine
2 Mowiol 50-98
solvant: eau
temperature - 45±0,2°C
ηsp. 10⁻²
C → g/100ml

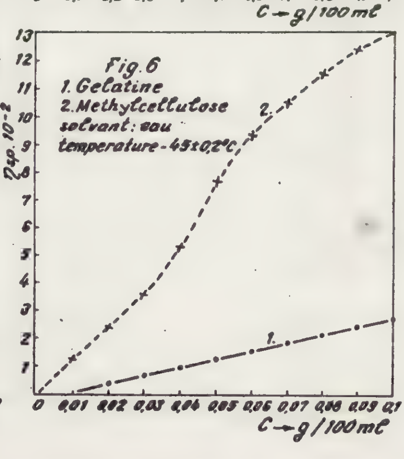
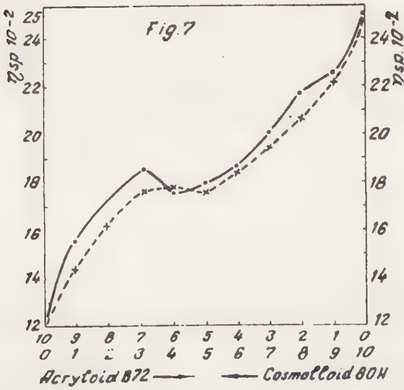
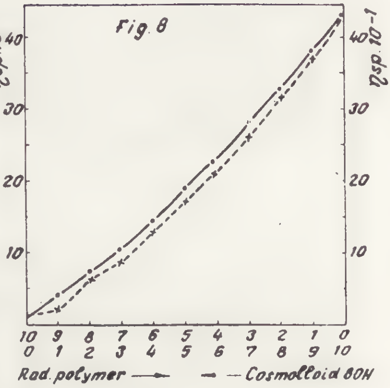
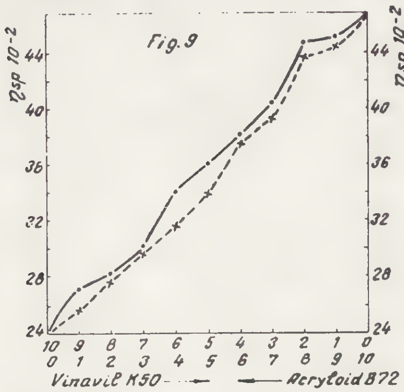
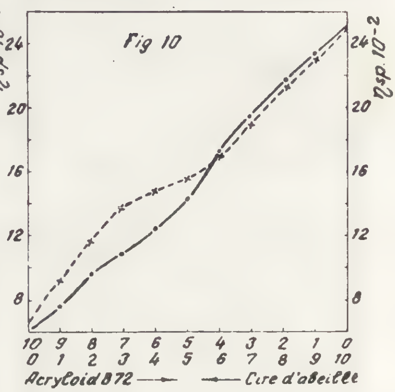


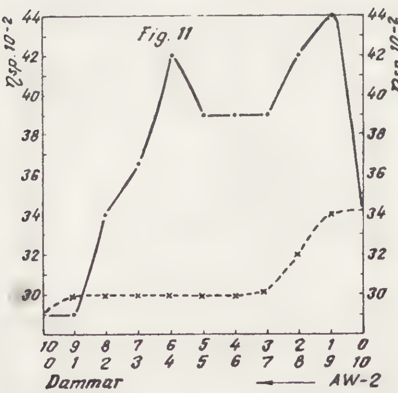
Fig. 6
1. Gelatine
2. Methylcellulose
solvant: eau
temperature - 45±0,2°C
ηsp. 10⁻²
C → g/100ml

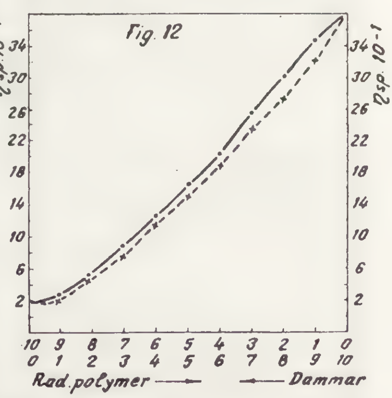












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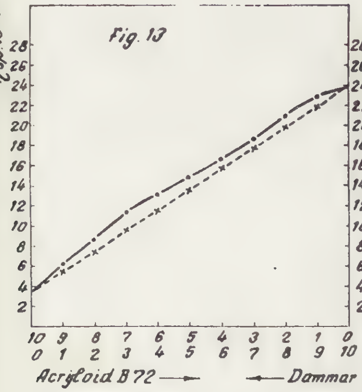
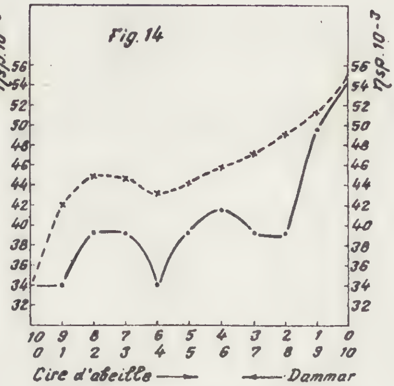
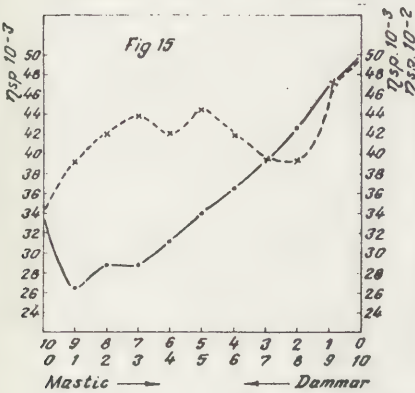
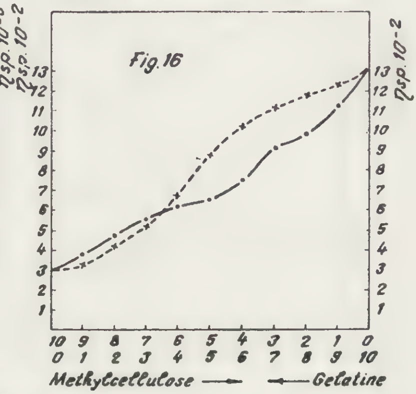
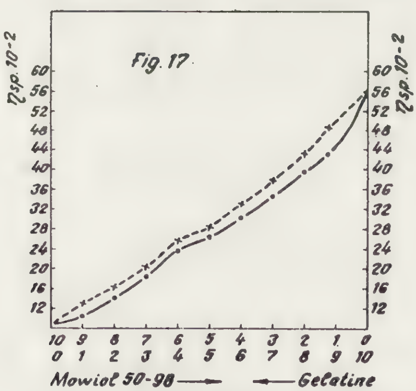
x- - - - - - courbe additive











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x------- courbe additive

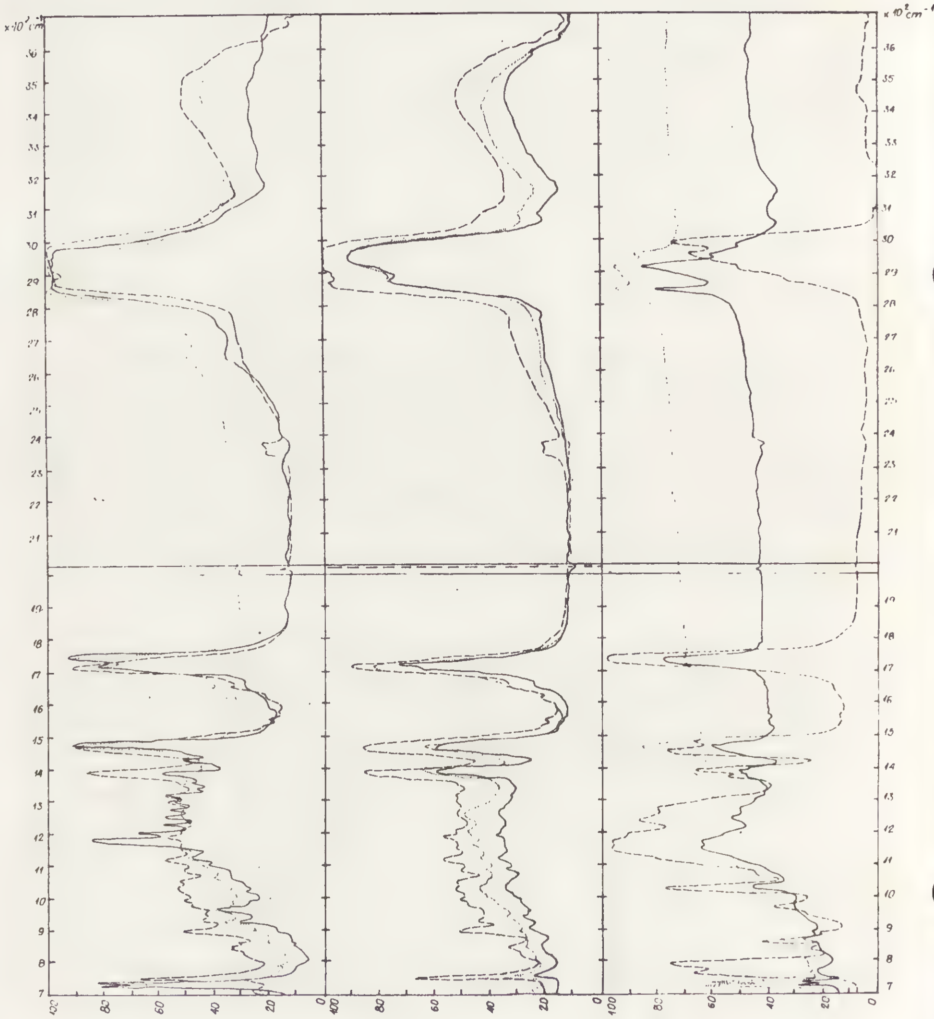

FIG 18

— Dammar - Cire d'abeille 1:1
--- Dammar
... Cire d'abeille

FIG 19

— Dammar-mastic 1:9
— Dammar
... Mastic

FIG 20

— Acryloid B72-Cosmolloid 80H 1:1
---- Acryloid B72
Cosmolloid 80 H

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USE OF GAMMA RADIATION FOR CONSERVATION PURPOSES IN CZECHOSLOVAKIA

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5th Triennial Meeting
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Abstract

A survey is given of the work currently in progress in Czechoslovakia in the field of applying the ionizing radiation to conservation of objects of art and museum collections. More particular attention is paid to a new complex radiation and chemical method of treatment of wooden objects attacked by insects or other harmful agents. The radiation disinfestation procedure developed in the Nuclear Research Institute at Řež effectively exterminates the wood-boring insects within the whole treated object, brings about a large economy of restorer and conservator handwork, provides a long-term preventive protection and does not influence the external appearance of the wood. Finally, an account is given of the project of Laboratory for Radiation Treatment and Chemical Conservation which is to be put into operation in 1979 at the Central Bohemian Museum at Roztoky near Prague and to apply the new method on a centralized large-scale basis.

Introduction

The considerable amount of damage due to ageing, atmospheric influence and other harmful factors of all kinds is nowadays threatening with destruction the rich stocks of objects and monuments of art and handcraft. The institutions charged with care about this cultural estate - the museums, galleries, archives, institutes - as well as thousands of amateurs and collectors have

become aware of the serious consequences of this threat and are looking for effective ways of redress or prevention.

The methods of conservation, though differing because of regional differences in conditions of damage, must always be in accordance with general principles of conservation. When appraising the applicability of methods of conservation one must consider the nature of the objects to be conserved whose cultural value greatly depends upon their authenticity. Any step during the process of conservation should therefore maintain the authenticity or, at least, the typical nature of the object. It is also necessary to provide for a complex care involving the protection of the collection items both in depositaries and during permanent or transient exhibitions.

The above requirements bring about the necessity to develop the specific creative activity of conservation on the basis of latest achievements in science and technology. Although the introduction of modern methods into the practice of conservation and restoration often has to cope with misunderstanding or even refusal, several progressive methods have recently been adopted. They include the radiation treatment of objects of art which aims at either eradicating harmful fauna and flora or petrifying the objects by radiation-induced polymerization.

Present situation in Czechoslovakia

One of the most burning problems in the care of monuments of art in Czechoslovakia is the harm done to objects made from organic materials such as paper, leather, natural fibre and, especially, wood by living organisms. The attack by destructive insects, fungi, moulds and bacteria becomes wide-spread and attains dangerous dimensions.

The specialists of the Consultation Centre for the Application of Ionizing Radiation at the Nuclear Research Institute (NRI) at Řež have tried, since 1974, to awake interest of relevant institutions and some museums in Czechoslovakia in applying radiation methods in the fight against the harmful agents mentioned above. Relying upon the results obtained in our country during investigations on the use of ionizing radiation against granary insects as well as on the work by the French group at CEN Grenoble [1,2,3], we have considered it most realistic in our conditions to start first the promotion of the radiation disinfestation and defungisation method and, after gaining experience, to tackle the radiation petrifaction method.

This strategy was based on an analysis of the actual situation of museum funds in Central Bohemia, one of the ten administrative districts in Czechoslovakia. Together with a number of specialized museums such as the National Museum or the National Technology Museum in Prague, this region involves over 50 regional and local museums. Most of these museums own collections from different branches such as archeology, history, history of art, ethnography, natural science etc. Their overall fund amounts up to 3 millions of items and includes both objects of art and museum pieces of documentary value. A rough estimate of the extent of attack by insects indicates that about a third of these objects is in actual or potential danger. Half of this number are wooden objects, the other half refers to objects made from paper, textile, leather, wicker or straw. Thus, in one single district of Czechoslovakia, about half a million collection items are waiting for the help against wood-boring insects.

These facts obviously seemed to warrant promotion of a research project on radiation disinfestation. Mo-

reover, the directory of the Central Bohemian Museum (CBM) at Roztoky near Prague - in the near vicinity of the NRI at Řež - quickly responded to the challenge by taking up an enthusiastic project of establishing a Laboratory for Radiation Treatment and Chemical Conservation. This Laboratory, equipped with an appropriate irradiation unit and a specialized laboratory for chemical conservation, would be able to treat attacked collection items from all museums of the district and, eventually, from other sources as well.

Since 1975, the radiation disinfestation method has been studied in detail and a complex radiation and chemical treatment procedure developed. During the same time, a team of the NRI projected the irradiation facility to be installed at the CBM. After financial means had been granted by the district authorities in 1977, the building at Roztoky began with the aim to put into operation, in 1979, a first irradiation chamber of its kind in the world - established outside a nuclear research centre and serving the purpose of centralized radiation treatment of objects of art and museum collections.

The method

In today's museum practice a considerable portion of collection items requires conservation and protection against insects, moulds and fungi. It is, however, practically impossible to achieve 100 % depth penetration, that is, to guarantee the protection, by means of any conventional insecticide or fungicide. This is true of most simple wooden objects, to say nothing of those having an original artistic surface finish such as painting, polychromy or tarsiatura.

The principal advantage of the radiation method lies exactly in the fact that the high-energy gamma radiation easily penetrates into the depth of the ob-

jects to be cured and safely destroys the harmful insects or other living organisms. The radiation dose necessary to exterminate all kinds of woodworms is about 250 Gy (formerly 25 krad; 1 Gy = 100 rad) [2,3,4]. Destroying moulds and fungi requires doses about twenty times higher - around 5 kGy; due to a synergic effect of heat, however, an elevated temperature of about 50°C has a sensibilizing influence of lowering the necessary defungisation dose to about 500 Gy [5].

The latter value of 500 Gy has been adopted as the nominal radiation dose for disinfestation to be used both in current service work at NRI and at the future CBM Laboratory. This dose is not injurious to both oil and tempera polychromies, [6] to glued tarsiatura and other common types of surface finish of ancient objects. As far as the wood itself is concerned, doses as high as 50 to 100 times the above value have no appreciable negative effect upon its physico-mechanical properties, nor on its outer appearance. Results of experiments aiming at verifying and demonstrating the validity of these postulates, suggested thus far by scarce literature data quoted above, will be published in the near future.

However, since the radiation treatment is basically curative but not preventive, i.e. it does not provide protection against a new attack, it is necessary, after irradiation, to furnish the surface of the treated object with a protective layer containing a persistent chemical insecticide. This preventive conservation, be it performed by spraying or coating, can, however, be literally "superficial" and need not even concern wood already protected by a layer of insect resistant material such as paint. Its task is not to kill, but to prevent the imago of a woodworm from laying new eggs or the dispersed spores of a wood-destroying fun-

gus from sprouting. A suitable mixture for this purpose seems to be a solution of pentachlorophenol and tributyltinoxide in a toluene-type solvent containing wax and/or damara resin. This mixture is capable of fixing the insecticide homogeneously dispersed in the surface layer for a considerable time without altering the appearance of the surface.

It is seen that the combined radiation-chemical treatment not only immediately stops the process of destruction of wood by insects and provides long-term subsequent protection against them, but, in contrast to most other conservation methods, fully corresponds to the requirements of the principle of unaltered authenticity, mentioned in the introduction.

In addition, work has begun in Czechoslovakia on radiation destruction of moulds attacking paper with a view to possible conservation of ancient books or archival materials. The investigations again concentrate on the utilization of combined effect of heat and radiation to lowering the necessary radiation doses to the level used for disinfestation. Though there exists large interest in a rapid introduction of this method, the importance of a thorough experimental verification must not be underestimated here having in mind the extreme sensitivity of the basic cellulose material towards radiation. The same is more or less true for the other potential adepts for radiation treatment such as ancient textile or leather.

A final method of extreme potential interest is the use of radiation for petrifaction of heavily damaged or quasi-destroyed wooden objects impregnated by a polymerizable resin-monomer system. This method, successfully developed in France [3,7,8] for both dry and water-logged wood as well as for stone, requires still more severe caution when applied to objects having a

surface finish. This is so because the polymerization doses vary between 10 to 50 kGy, i.e. in the region where secondary effects on radiation-sensitive components such as dyes or binding agents may occur. This circumstance has greatly hindered the application of the method in Czechoslovakia since it necessitates detailed investigations to be made by a multiprofessional team involving restorers, conservators, testing specialists and radiation chemists and technologists. Only preliminary studies are thus far in progress at the NRI and a few other laboratories. Work done in the NRI uses doses in the range from 0.5 to 100 kGy and both subjective and objective methods of testing; it is presently concentrated to radiation effects on i) colour changes of original paintings and polychromies and ii) adhesion strength, impact and bending resistance and other properties of simulated chalk base layers bonded by gelatine, caseine or egg albumen.

The irradiation facility at CBM

Next we shall describe in some detail the technical parameters of the irradiation unit planned as a part of the Laboratory for Radiation Treatment and Chemical Conservation to be built at the CBM. The Laboratory will be located in the basement of the administrative building of the Museum - former cellar of a small XVIIth century brewery belonging to the Roztoky Castle. One of the basement rooms will serve as the irradiation chamber (see Fig. 1). The original stone- and brick--work of the one-meter walls of this room needs but a modest concrete walling to be added in order to obtain sufficient shielding capacity. Only the vault must be completely rebuilt using 125 cm of ordinary concrete. Neighbouring rooms provide space enough for an entrance corridor, control and manipulation areas, and a chemical laboratory for preventive conservation.

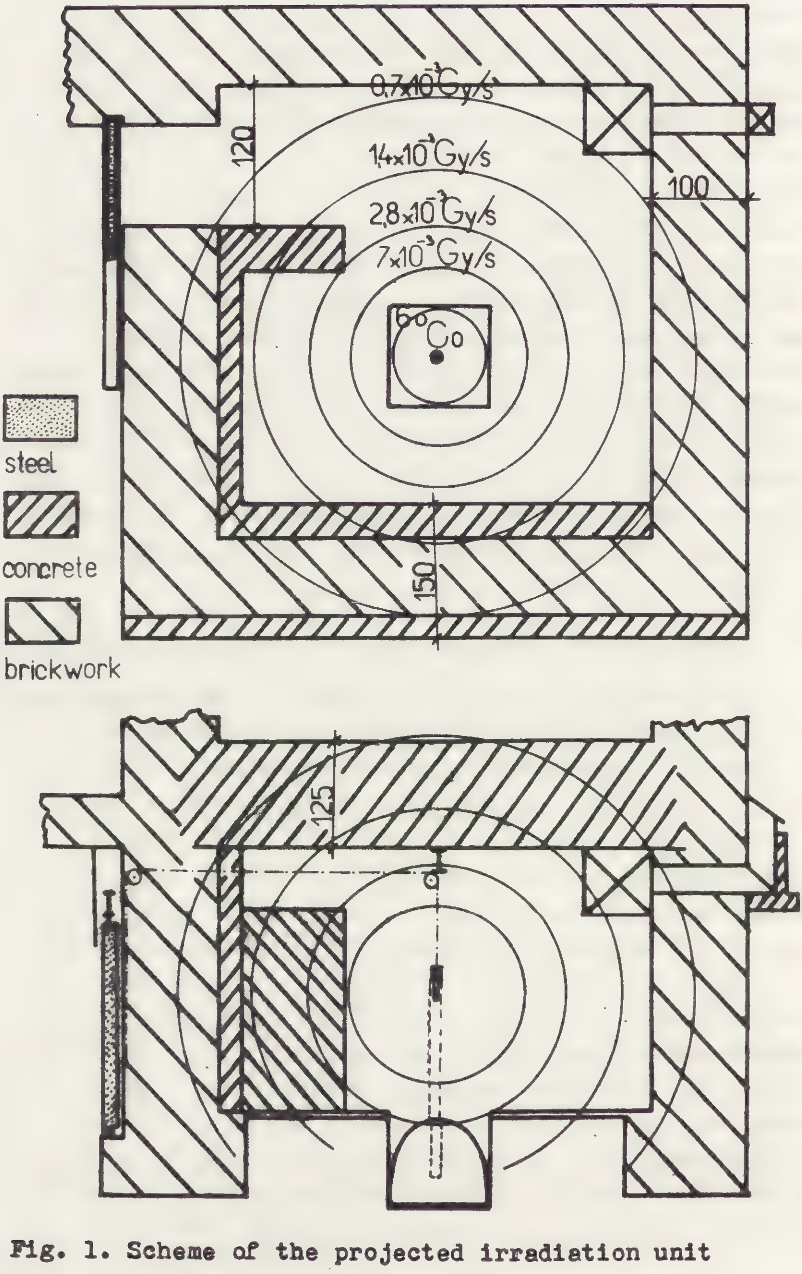

Fig. 1. Scheme of the projected irradiation unit

The irradiation chamber has the dimensions of 5 x 4.5 x 3 m. It is equipped with a ^{60}Co-isotope gamma source of 75 TBq (2 kCi) initial activity. The source unit is based on a reconstructed standard transport lead container of the KIZ-10000 type produced in the USSR. A set of two to three cylindrical cobalt sources, encapsuled in stainless steel and fixed to the bottom of a lead plug, may be pulled up to the irradiation position at a height of 50 - 130 cm above the ground by means of a steel rope movable on pulleys. The loading of the container will be performed at the NRI so that the transport and the installation at the CBM will present no practical problems of radiation safety.

The entrance to the irradiation chamber is through a 15 cm cast-iron sliding door, shielded in addition with a concrete ledge placed within the chamber to form a simple labyrinth. The dimensions of the chamber walls, vault and door are chosen so as to ensure radiation safety of the personnel during all operations and to allow for up to threefold increase of the source activity. The safe operation is further ensured by a combined electro-mechanical interlocking of the control mechanisms designed to prevent opening the entrance door unless the cobalt source is hidden in the container or pulling the source up unless the door is closed and no person present in the chamber. Furthermore, a TV set will serve to monitor the source area and to check the correct operation of the source mechanism. Finally, two ventilators having a total effective exhaustion power of 300 m^3 per hour will provide for the necessary removal of harmful products of the air radiolysis, i.e. ozone and nitrogen oxides.

The objects presented for treatment will be displaced in two concentrical files corresponding to irradiation times about 24 and 48 hours respectively. In the meantime, objects already irradiated will undergo,

preventive conservation. Under the assumption of two cycles per week and 40 working weeks per year, the total number of average-size objects (e.g. statues of 80 cm in height) treated per year is estimated at two thousands. This is quite in accord with the expected extent of demand having in view the alarming situation analysed above. The prize for treatment evaluated on this basis represents a negligible fraction of usual restoration costs. The economy of handwork gained due to the fact that the restorer will no more need to care for careful and lengthy conservation of the object by conventional methods is enormous indeed.

It is hoped that the regular operation of the new facility will corroborate the surmised technical and economical advantages of the large-scale application of the new method and serve as a steady stimulus for more intense development of other related and potential applications both in Czechoslovakia and elsewhere.

Acknowledgment

Fruitful technical cooperation of J. Majer, Head, and the staff of the Construction Department of the NRI and continuous support of J. Bednář, Head of Ionizing Radiation Division, are gratefully acknowledged. Thanks are also due to B. Kounovská, Director of the CBM, for permission to publish data on the new Laboratory.

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ADAPTATION A LA DESINFECTION DE LA MOMIE DE RAMSES II DU PROCEDE DE RADIO-STERILISATION GAMMA

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ADAPTATION A LA DESINFECTION DE LA MOMIE DE RAMSES II DU PROCEDE DE RADIOSTERILISATION GAMMA

C. de Tassigny et M. Brouqui

RESUME

Une adaptation du procédé de radiostérilisation gamma a permis de mettre au point la méthode de désinfection de la momie de RAMSES II à température, pression et hygrométrie ambiante sans apport de produit chimique.

Par des études préalables on a fixé à 1,8 Mrd la dose de destruction des espèces contaminantes et vérifié l'inocuité de cette dose sur les constituants de momies d'étude. Les conditions d'irradiation de ces momies ont été déterminées théoriquement et l'expérience a confirmé les indications du calcul. Un dispositif particulier a été mis en place pour préserver la momie d'une nouvelle contamination.

Peu d'objets en matière organique résistent à l'épreuve de plusieurs millénaires. Certains matériaux périssables constituent cependant des exceptions parce qu'ils sont conservés dans des conditions particulièrement favorables, dans un milieu aqueux par exemple, qui permet la sauvegarde du bois d'épaves sous marines.
D'autres exceptions sont représentées par des bois secs égyptiens maintenus à l'abri de chambres funéraires dont l'ambiance climatique est stable et peu humide.
L'altération de ces matériaux est faible pendant quelques millénaires, mais ils se dégradent beaucoup plus rapidement dès leur mise à jour quand l'équilibre avec leur milieu de préservation naturel est rompu.

Il en est de même pour les momies.
Celles-ci ne proviennent pas exclusivement d'Egypte. Des corps humains mais également d'animaux ont été momifiés par millions (1). Les procédés sont variés : un séchage dans les conditions d'hygrométrie très particulières des sables désertiques peut suffire à conserver les corps (2). Il semble cependant que l'évolution des coutumes rituelles en Egypte ait entraîné la mise au point de procédés plus élaborés de conservation : la déshydratation du corps avec une composition saline, le natron (3), est complétée par un embaumement avec des résines végétales (4) (5).

En Egypte, ma momification, est souvent achevée par un bandelettage et les sarcophages constituent autant de protections supplémentaires contre les agressions potentielles.
L'exposition d'une momie dans de mauvaises conditions de conservation provoquées par une chaleur ou une humidité excessive favorise le développement de microorganismes et l'attaque des insectes, entraîne la putréfaction des constituants organiques et la dégradation

physique du corps momifié.
La mise en évidence d'une évolution rapide de l'état d'altération de la momie de Ramsès II (6), conservée dans la salle des momies du Musée du Caire (7), a fourni l'occasion d'approfondir les causes de son altération et de mettre au point un procédé de désinfection approprié.

CAUSES D'ALTERATION

La momie de Ramsès II a été découverte par MASPERO en 1882 dans une tombe de Haute Egypte, à Deir-el-Bahari. Après avoir été conservée pendant près de trois mille ans dans cette cachette elle fut transportée au Caire peu après sa dédouverte et débandelettée. Elle fut exposée plus tard au Musée du Caire, dans une vitrine en verre non étanche. Le milieu ambiant s'est révélé favorable au développement parasitaire d'insectes et de champignons qui ont porté atteinte aux matières organiques, à la résine d'embaumement ainsi qu'au textile des bandelettes résiduelles et du linceul.

L'étude des causes d'altération a été menée au Muséum d'Histoire naturelle de Paris (8). Les examens ont révélé que la momie avait subi une attaque ancienne de larves d'insectes (9).
Aucune bactérie pathogène n'a été décelée (10).
L'analyse des foyers d'infection récents, en partie visibles sur le corps et développés également à l'intérieur de la cavité abdominale, a révélé la présence d'une population fongique dense et variée : il s'agissait de plusieurs dizaines d'espèces de champignons généralement observables dans les régions tempérées ou tropicales, qui peuvent se développer dans des conditions d'hygrométrie et de température très étendues (11).

CRITERES DE DESINFECTION

Le choix d'un traitement de désinfection était assorti d'exigences très strictes qui se traduisaient par la nécessité d'appliquer un procédé de désinfection dans des conditions de pression, température et hygrométrie ambiante sans aucun apport de produit chimique désinfectant. A l'ensemble de ces conditions s'ajoutait également celle de maintenir après traitement la stérilité de la momie dans sa vitrine de présentation au Musée.

Les méthodes classiques de désinfection par la chaleur ou par gaz ne pouvaient pas répondre favorablement à l'ensemble des critères ainsi définis*.

L'irradiation par rayonnement gamma est une technique de désinfection appliquée depuis plusieurs années à l'échelle industrielle et répond bien aux impératifs déjà cités :

---

* L'oxyde d'éthylène est un gaz non toxique pour ces constituants mais son utilisation nécessite de procéder sous vide.

- pratiquée correctement, l'irradiation n'entraîne pratiquement pas d'élévation de température**.

- aucun produit chimique n'est utilisé.

- le traitement s'effectue à température, pression et hygrométrie ambiante.

- le rayonnement gamma utilisé provient de la désintégration des noyaux de cobalt 60 ; l'énergie de ce rayonnement (1,17 et 1,33 MeV) est inférieure au seuil des réactions photonucléaires. Il ne peut donc pas induire de radioactivité dans les objets ainsi traités.

- ce rayonnement est très pénétrant pour des matériaux de faible densité : aucune zône du corps irradié n'est hors d'atteinte et l'on peut vérifier par des mesures appropriées que la dose de décontamination a bien été reçue.

- un objet contaminé peut être traité dans son emballage.

Le procédé répond bien dans son principe aux exigences de désinfection d'une momie dans son enceinte d'exposition. Le caractère nouveau et spécifique de ce traitement a cependant nécessité des études préliminaires afin de :

- déterminer la valeur de la dose de désinfection.

- vérifier l'inocuité de cette dose sur les constituants de la momie.

- prévoir les conditions d'irradiation à partir d'un modèle de calcul.

- vérifier expérimentalement la validité de ce modèle.

- définir le conditionnement et son mode d'utilisation pour éviter une recontamination de la momie durant les opérations de transport et d'exposition.

DOSE DE RADIOSTERILISATION

La valeur des doses d'irradiation gamma insecticide, bactéricide ou fongicide résulte des nombreuses recherches menées dans ce domaine (12). Actuellement, plus d'une centaine d'installations industrielles dont la capacité est de l'ordre de 60 m^3/jour radiostérilisent du matériel médical,quelque fois des produits alimentaires (13). Les doses de stérilisation, qui dépendent de la nature du produit à traiter vont de 2,5 à 8 MRads.
Mais les conditions habituelles d'irradiation industrielle doivent être ajustées pour la désinfection d'une momie dont les éléments constitutifs, la nature de la contamination, les dimensions et les matériaux d'emballage diffèrent des caractéristiques d'objets d'usage courant, stérilisés dans des volumes normalisés.

** La puissance dissipée dans le volume irradié est très faible dans les conditions de l'expérience : pour une intensité de dose voisine de 150 krd/h, elle est inférieure au milliwatt par gramme.

Afin de limiter les interactions possibles du rayonnement sur les constituants organiques de la momie on a cherché une dose minimale de rayonnement gamma suffisante pour détruire sa contamination majeure par des champignons.
Les doses de stérilisation bactéricide et fongicide étant 50 fois supérieures aux doses de désinsectisation, il n'était pas utile de chercher à connaître une dose minimale de destruction d'une éventuelle contamination par des insectes.
A partir des prélèvements effectués sur et dans la momie par le laboratoire de cryptogammie du Muséum d'Histoire Naturelle de Paris, les souches de plus de 60 espèces de champignons ont pu être isolées, cultivées et transmises au Centre de Recherches sur la Conservation des Documents Graphiques.

Le comportement au rayonnement gamma de 36 souches de champignons considérés comme les responsables les plus fréquents de la détérioration des matériaux graphiques (papiers, parchemins, cuirs) était déjà connu grâce à une étude menée par ce laboratoire avec la collaboration du Centre d'Etudes Nucléaires de Grenoble (14).

Les doses de destruction de ces champignons avaient été étudiées sur des cultures sur substrat de papier, de cuir, et de parchemin afin de se placer dans des conditions réelles de désinfection de documents graphiques.
La dose létale de l'ensemble des champignons avait été évaluée à 1,8 Mrd.

Ces substrats présentaient une analogie avec les constituants de la momie (corps et bandelettes) qui supportaient une activité fongique similaire.
Une partie de la flore cryptogammique de la momie (14 souches) était comprise parmi les champignons déjà étudiés.

Il restait à vérifier que les autres souches communiquées par le laboratoire de cryptogammie étaient détruites par cette dose de 1,8 Mrd.

Des cultures de ces champignons sur substrats (parchemin, cuir, lin et gélose) ont été irradiées à 1,8 Mrd avec un débit de dose moyen inférieur ou égal à 200 krd/h.
On a vérifié que toutes les cultures étaient stérilisée dans ces conditions (15).

Compte tenu de l'activité maximale de la source disponible et de l'homogénéité souhaitée de l'irradiation, le débit de dose moyen à délivrer dans la momie a été fixé à 150 krd/h*.

---

* Pour une source donnée le débit de dose croît lorsqu'on se rapproche de la source. Il en est de même de l'hétérogénéité de la dose.

VERIFICATION DE L'INOCUITE DE LA DOSE DE STERILISATION

Si les données bibliographiques sont abondantes en ce qui concerne le radiotraitement des denrées alimentaires et les produits médicaux, (12), (16), (17) , par contre les renseignements bibliographiques sur les effets de l'irradiation gamma de constituants secs et très anciens d'une momie sont à notre connaissance inexistants et la vérification de leur comportement a nécessité une étude particulière.

Aucun prélèvement n'était possible sur la momie de Ramsès II. Seuls quelques fragments de cheveux et de bandelettes étaient disponibles. Pour vérifier les effets éventuels de ce traitement sur un ensemble représentatif des principaux constituants d'un corps momifié, l'échantillonnage a été complété par des prélèvements effectués sur d'autres momies du laboratoire d'anthropologie du Musée de l'Homme et sur des cadavres récents.
Chaque échantillon a été séparé en deux fragments :

Le premier lot a été irradié dans les conditions définies puis envoyé aux laboratoires spécialisés pour comparaison avec les fragments témoins non irradiés.

Des échantillons de cheveux, poil, peau, muscle, vertèbre provenant d'une momie péruvienne du Musée de l'homme ont été soumis à des examens histologiques (18). Les mêmes examens ont été pratiqués sur des fragments de peau, foie, poumon, rate, rein, coeur, os provenant d'un cadavre récent (18).
Des prélèvements autour de l'os illiaque d'une momie égyptienne du Musée de l'Homme ont été examinés par microscopie optique et électronique (19).
Des cheveux de la momie de Ramsès II et d'autres momie déposées au Musée de l'Homme ont été observés en microscopie optique et soumis à des contrôles mécaniques (20). Les dents d'une momie péruvienne ont été étudiées en microscopie optique (21). Des fragments de bandelettes de la momie de Ramsès II et d'une autre momie égyptienne ont subi des contrôles mécaniques et chimiques appropriés (22), (23).

Ces examens comparatifs ont démontré l'absence d'altération significative des échantillons irradiés dans les conditions déjà définies.

DEFINITION DU MODE OPERATOIRE DE TRAITEMENT

A l'instar des traitements de désinfection par gaz, l'utilisation du rayonnement est un procédé curatif : l'objet stérilisé peut être infecté à nouveau dès qu'il est placé dans une atmosphère contaminée. Le rayonnement gamma assure la désinfection au travers d'un emballage et d'une enceinte fermée, étanche.

L'étanchéité de cette enceinte vis à vis des agents de contamination (insectes, bactéries, champignons) garantit la stérilité ultérieure des objets qui y ont été désinfectés.
Pour préserver la momie après traitement il fallait être assuré qu'elle demeure en atmosphère stérile, donc l'irradier par exemple dans sa vitrine d'exposition. Mais il était nécessaire de la caler dans son sarcophage et de fixer l'ensemble dans cette vitrine pour la maintenir fermement durant son transport. Cette opération nécessitait cependant en fin de transport d'ouvrir la vitrine pour enlever les matières d'emballage incompatibles avec les conditions de présentation.
Ces exigences contradictoires ont été satisfaites en effectuant l'irradiation de l'ensemble vitrine-sarcophage-momie-matière de calage dans une enveloppe souple et étanche (24).
Ce dispositif transparent analogue à une boîte à gants offrait la possibilité de manipuler à l'intérieur de son volume les objets maintenus en atmosphère stérile.
Tous ces matériaux ainsi que les accessoires nécessaires aux travaux à l'intérieur de l'enceinte d'isolement devaient bien entendu se comporter sans dommage à l'irradiation gamma. Un schéma simplifié résume les différentes phases de l'opération (tableaux 1 et 2)

CALCUL DES CONDITIONS D'IRRADIATION

Les conditions habituelles d'exploitation des cellules d'irradiation ne convenaient pas à l'irradiation homogène d'une momie de grande taille (1,72 m) :
une modification de l'arrangement des sources de cobalt 60 s'avèrait nécessaire pour obtenir une plus grande homogénéité du champ de rayonnement dans le volume occupé par la momie.

Cette recherche d'une bonne homogénéité du champ de rayonnement dans l'air était une première condition pour délivrer sur et dans la momie une dose d'irradiation relativement homogène.
Les matériaux à irradier constituent un ensemble complexe :

- les formes géométriques de la momie, du sarcophage, des matières de "calage" ne sont pas simples.

- chacun de ces matériaux hétérogènes constitue un écran d'épaisseur, de densité et de forme différente dont les constantes nucléaires sont inconnues.

On a conçu un modèle de calcul permettant de connaître la répartition des doses dans le volume de la momie. La simulation a consisté à réduire une image de la momie et de son emballage en formes géométriques simples (figures 1 à 4). Les constantes nucléaires des matériaux ont été estimées d'après les mesures effectuées sur d'autres momies.
Ce modèle a permis de :

- prévoir une disposition des sources adaptée aux conditions d'irradiation (1,8 Mrd, 150 krd/h moyen) et à l'homogénéité de la dose désirée.

- calculer l'intensité de la dose en tout point de la momie selon sa position par rapport aux sources et la présence des matières absorbantes (25).

VERIFICATIONS EXPERIMENTALES

La validité des approximations faites pour construire ce modèle de calcul a été vérifiée sur deux momies d'étude provenant du Musée de peinture de Grenoble et du Laboratoire d'anthropologie du Musée de l'Homme. Durant l'irradiation, leur conditionnement était analogue à celui de la momie de Ramsès II. Les contrôles de doses ont été effectués simultanément par deux méthodes dosimétriques ("red perspex" et "triacétate de cellulose") sur et dans les momies.
Un tableau comparatif (tableau 3) regroupe à titre d'exemple les doses calculées et mesurées pour l'irradiation de la momie d'étude du Musée de l'Homme.
On a vérifié ainsi le bon accord du calcul avec l'expérience (sans chercher à obtenir dans cette expérience une dose de 1,8 Mrd).

TRAITEMENT DE LA MOMIE DE RAMSES II

Caractéristiques de l'irradiation :

Activité des sources : 160.000 Ci

Durée d'irradiation : 12h40 mm (On a fait pivoter horizontalement la caisse de 180° à mi-irradiation pour assurer l'homogénéité de la dose).
Des dosimètres (red perspex) positionnés autour de la momie avant irradiation ont été contrôlés après traitement :

dose minimale reçue par la momie : 1,8 Mrd.

Coefficient de surdosage : 1,33 (rapport de la dose maximale à la dose minimale).

Précision des mesures : voisine de 10 %

RADIOSTERILISATION D'AUTRES MOMIES

Le procédé de radiostérilisation gamma a été adapté à la désinfection d'une momie dans sa vitrine d'exposition, sans rupture de l'état de stérilité obtenu par l'irradiation.
Aucune contamination de la momie n'est ensuite possible tant que la vitrine reste fermée.
Ce mode opératoire peut être appliqué à d'autres momies qui sont soumises aux mêmes causes d'altération et dont les éléments constitutifs sont analogues.
La nature des conditions de conservation du Musée du Caire, propices au développement des moisissures, a rendu nécessaire la mise au point d'un procédé complexe de déballage et de présentation. Il semble toutefois possible de simplifier l'opération si l'on peut éviter d'utiliser le dispositif "boîte à gants".

- désinfection d'une momie conservée dans une "réserve"

Les momies entreposées dans les réserves peuvent être simplement radiostérilisées dans une enveloppe étanche (une gaine en matière plastique souple et transparente par exemple).
Après irradiation, la momie peut être déposée ainsi dans son entrepôt. Stérile dans son emballage, elle ne peut plus être contaminée tant que l'enveloppe reste fermée.

- <u>désinfection d'une momie "d'exposition"</u>

Le responsable de la conservation d'une momie peut juger le milieu ambiant d'exposition suffisamment sain (salle ou vitrine désinfectée) et stable (conditions climatiques contrôlées) pour choisir une présentation dans une vitrine non stérile. La désinfection de la momie a lieu, suivant le même principe, dans une enveloppe étanche. Mais si la momie est sortie de son emballage après irradiation, elle n'est plus à l'abri d'une contamination ultérieure.

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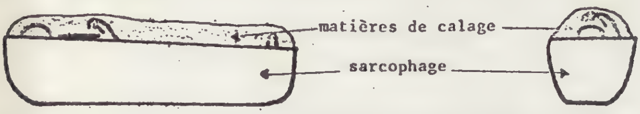
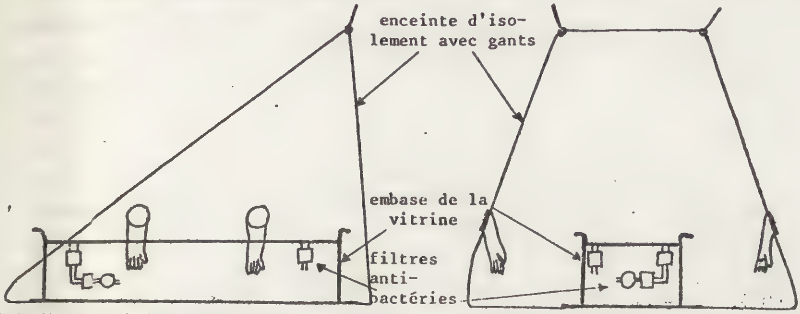
TABLEAU 1 - Synoptique du traitement de la momie de RAMSES II

1. Calage de la momie dans son sarcophage - Mise en place des dosimètres



2. Introduction de l'embase de la vitrine dans l'enceinte d'isolement



3. Introduction du sarcophage. Calage dans la vitrine. Fermeture de la vitrine
Raccordement d'un dispositif filtrant de mise en équipression avec l'extérieur

4. Mise en caisse après fermeture de l'enceinte d'isolement.

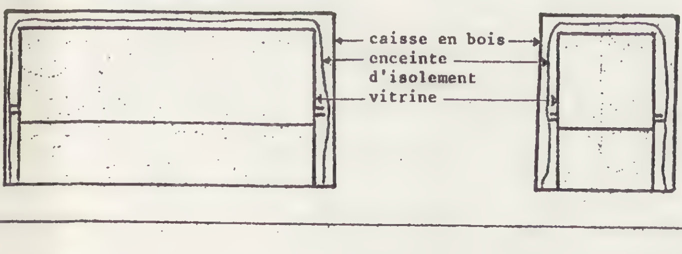
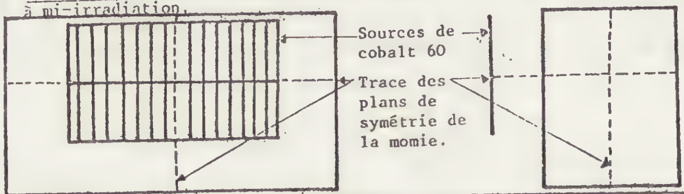
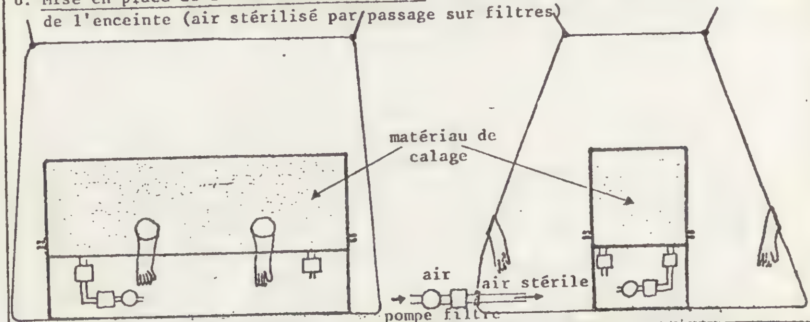


TABLEAU 2 - Synoptique du traitement de la momie de RAMSES II

5. Irradiation - Positionnement de la caisse. Retournement horizontal de 180° à mi-irradiation.



6. Mise en place de la cellule d'isolement - Ouverture de la caisse - Gonflement de l'enceinte (air stérilisé par passage sur filtres)



7. Déballage - Manipulations en milieu stérile : Dépôt du couvercle, des matériaux de calage, des dosimètres, fermeture du couvercle.

8. Présentation - Enlèvement de l'enceinte d'isolement - Habillage de l'embase.

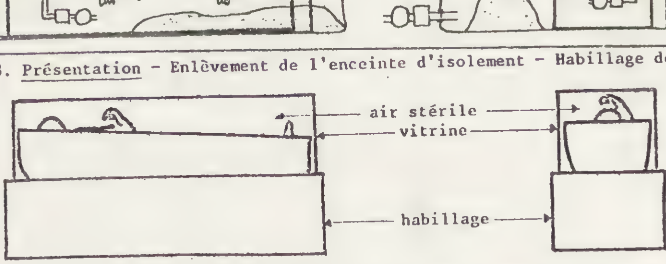


TABLEAU 3 – Comparaison après irradiation des doses calculées avec les valeurs observées en différents points d'une momie d'étude – Doses en Mégarads.

	Dose minimum mesurée Dm	Dose maximum mesurée DM	Dose moyenne mesurée $\bar{D}$	Dose calculée Dc	Ecart relatif %
pied, axe	2.311	2.500	2.406	2.194	+ 8.8
talon	2.271	2.571	2.421	2.158	+10.8
pied gauche	2.424	2.614	2.519	2.439	+ 3.2
genou droit	2.432	2.618	2.525	2.494	+ 1.2
genou axe	2.588	2.768	2.678	2.541	+ 5.1
genou gauche	2.421	2.696	2.559	2.605	– 1.8
main droite	2.358	2.578	2.468	2.115	– 1.9
ventre	2.362	2.586	2.474	2.504	– 1.2
cavité d'éviscération	2.316	2.662	2.489	2.341	+ 5.9
main gauche	2.482	2.654	2.568	2.654	– 3.3
épaule droite	2.589	2.864	2.727	2.647	+ 2.9
sternum	2.446	2.618	2.532	2.546	– 0.6
épaule gauche	2.900	3.121	3.011	2.952	+ 1.9
oreille droite	2.732	2.581	2.477	2.368	+ 4.4
nez	2.272	2.454	2.363	2.347	+ 0.7
oreille gauche	2.395	2.650	2.523	2.396	+ 5.0
crâne (occipital)	2.060	2.268	2.164	2.010	+ 3.0

$$\boxed{\% = 100 \ \frac{\bar{D} - D_c}{\bar{D}}}$$

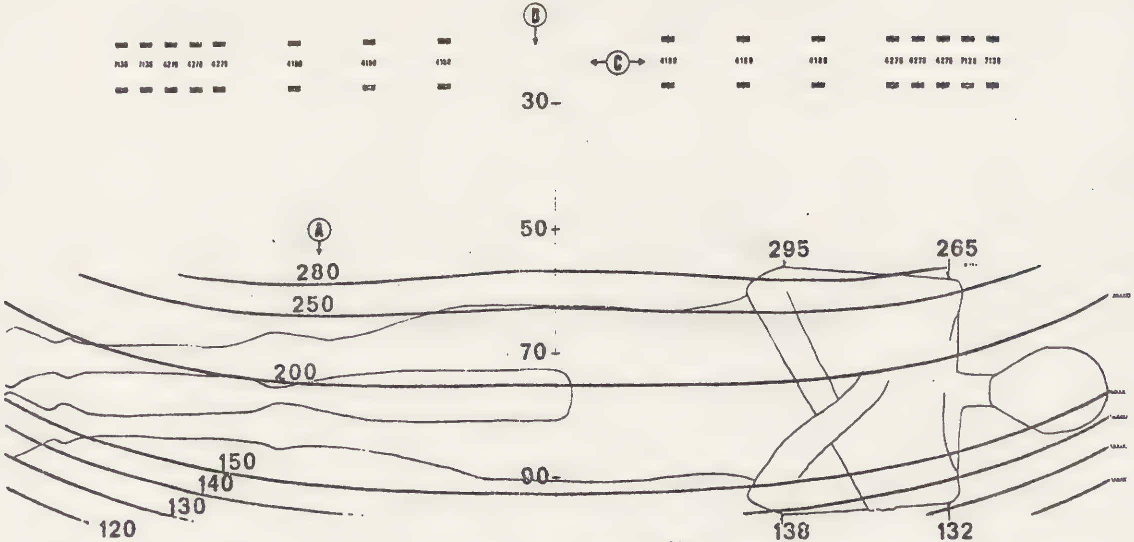
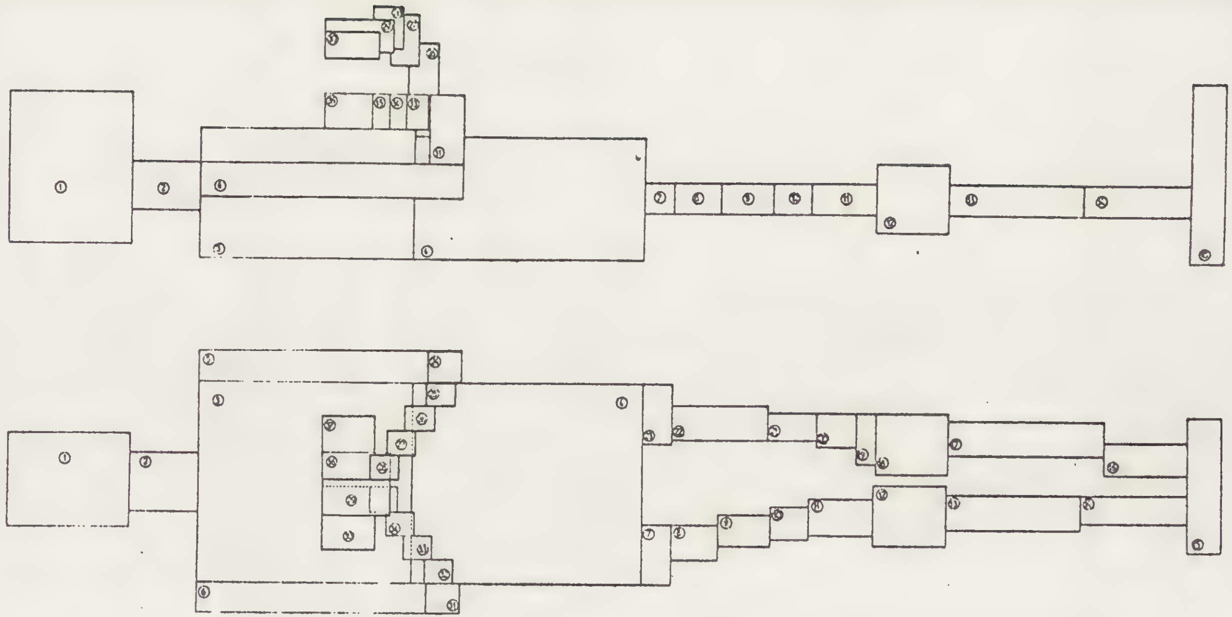


Fig. 1 - Exemple d'une disposition particulière des sources de ^{60}Co et de l'allure du champ de rayonnement qui en résulte, dans l'air.

A. Valeurs en kilorads/heure des intensités de dose sur la silhouette de la momie de RAMSES II.
B. Distances, en cm, au panneau porte-source.
C. Activité en Curie. Chaque source est représentée par un rectangle plein.



<u>Fig. 2</u> - Modèle de calcul de la momie de RAMSES II obtenu à partir de photographies et de mesures faites sur un squelette de même taille.

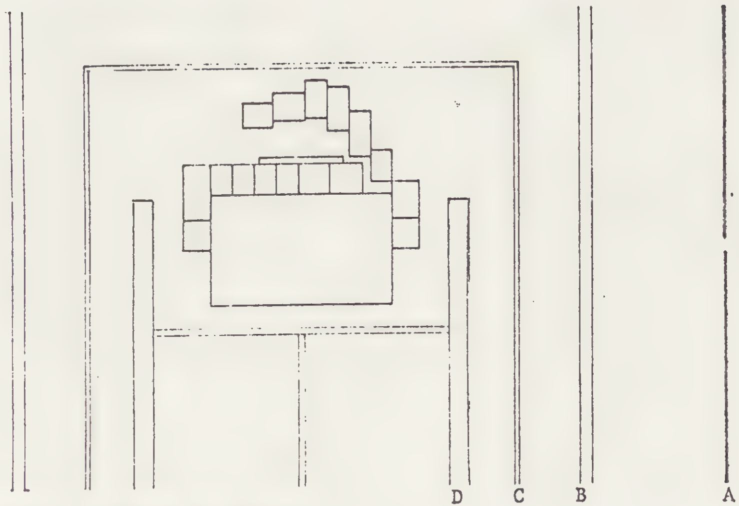


Fig. 3 - Epure de calcul.
Coupe transversale de la momie placée dans son emballage d'irradiation.
Seules sont représentées les parois suceptibles de freiner le rayonnement.

A. Sources.
B. Caisse de transport.
C. Vitrine de présentation.
D. Sarcophage.

LIGHTING AND AIR CONDITIONING

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Programme 1975-1978

Control of lighting and air conditioning for preventive conservation, with special emphasis on methods which are cheap, maintenance-free, require no unusual skills, and are economical in energy use.

The coordinator invites contributions in this field for selection for the next meeting of the Conservation Committee.

78/18/1

CLIMATE CONTROL POLICY

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ICOM Committee for Conservation

5th Triennial Meeting

Zagreb, 1978

CLIMATE CONTROL POLICY

Garry Thomson

Abstract

While by now many museums have installed air conditioning, maintenance is in general bad to appalling, to the extent of endangering the collection in many cases.

Class I and class II air-conditioning specifications are suggested, and the importance is stressed of using correctly the two basic instruments: the light meter and the wet-and-dry-bulb hygrometer.

There should always be a member of the conservation/curatorial staff with specific responsibilities as climate-control officer.

Research should now be directed towards cheaper and more easily maintained systems of climate control than the present air-conditioning systems.

INTRODUCTION

Looking back over the recent history of conservation, it would appear that great progress has been made in the installation of climate and lighting control in museums.

It is true that the Dark Ages of conservation, when museum directors were both ignorant of and totally uninterested in the technical needs of their collections, and moreover frequently put themselves into the hands of designers and architects equally ignorant, that period is now hopefully drawing to a close.

But in spite of this, prospects for the future safety of our cultural posessions are uncertain. Our critics might well object that our museums are now being filled with massive quantities of noisy and expensive machinery and with electronic devices which make the result of pressing even a simple light switch unpredictable.

What has gone wrong?

The answer is of course to be found in a mixture of causes, which we must now try to disentangle.

THE BASIC AIMS OF CLIMATE CONTROL

Without going into anything like full detail, we may

set Class I and Class II aims, Class I being a top-grade specification and ClassII having the aim of reducing the worst climate damage relatively cheaply and simply.

Class I

RH (Relative Humidity) to a set level day and night throughout the year within ±5%. The set level is commonly within the range 50 to 55% RH. Certain objects, particularly unstable metals, may require special conditions.

Ultraviolet radiation to be removed from daylight and from fluorescent lamp light. Maximum permissible level 75 μW/lumen.

Illuminance not to exceed set levels. A widely used recommendation is 150 lux for moderately sensitive materials (e.g. oil paintings), and 50 lux for sensitive materials (watercolours, textiles etc.). Daylight requires automatic control equipment.

Particulates to be removed with air filters, thus necessitating a ducted system of air conditioning, which is already required for full RH control. A suitable specification for the air filter: at least 65% efficiency on the Methylene Blue, Dioctyl phthalate or Sodium Flame Tests.

Air Pollution (gaseous). Sulphur dioxide and the nitrogen oxides to be removed, using activated-carbon or other suitable filters. Suggested specification: sulphur dioxide and nitrogen dioxide each reduced to below 10 μg/cu.m. Ozone reduced to trace levels with the same filter(0-2 μg/cu.m).

Class II

Class II assumes no ducted system of air conditioning and no automatic control of daylight. Control of RH is either by humidification (in winter-heating climates) or dehumidification (in the humid tropics or other damp situations).

RH to be kept away from the danger levels for mould growth (about 65 or 70%) and for embrittlement (about 40 to 45%).

Ultraviolet radiation to be removed as before.

Illuminance. It is possible to limit artificial light to 150 lux without undue difficulty or expense, but the 50 lux situation depends on ensuring adaptation of the visitor's eyes before entry to the exhibition space, and also on absence of glare. The worst excesses of daylight can be avoided by cutting out direct sunlight, vigilant use of blinds, constant surveillance with a light meter, and careful siting of the most sensitive exhibits.

INSTALLATION OF AIR-CONDITIONING EQUIPMENT

So much of the air conditioning in office and factory turns out to be air conditioning in name only. The equipment is run within very wide limits, dictated only by the volume of complaints coming in from the occupants of excessive heat or cold.

Before accepting tenders for installation, the museum ought to be convinced (a) that the equipment will be run at a much higher standard than is accepted in

offices, and (b) that the necessary standard of maintenance can be arranged.

In my own experience and that of many of my colleagues, the crux of the whole matter lies in maintenance. Cheap equipment can perform wonders in skilled hands, but even a Rolls Royce will soon be ruined by clumsy and incapable maintenance engineers.

Evidence for extremely poor maintenance is world-wide in museums.

MAINTENANCE

In an era of rapidly changing technology, to use an often-quoted phrase, progress is rapid in some areas and lags in others. New techniques produce unforeseen problems. There is just such a lead-and-lag situation in museums. Whereas a decade or so ago electricians were not required to understand anything more complicated than a relay, they are now faced with electronic circuitry controlling the lighting. A heating and ventilating engineer, however delicate his touch on the damper control, is baffled by the hygrometric chart. To compound the difficulty, instead of having risen following the spread of education, the standard of competence actually seems to have declined.

We now have staff in charge of air-conditioning equipment who could not even define RH, and other whose job is to change the paper on recording hygrometers who have not the least idea how to check their calibration, or indeed why they should be calibrated, and so the job never gets done.

The first task, therefore, is to ensure that the maintenance engineers are of a high enough calibre to look after the equipment which has been installed: not just to keep it alive but to keep it running at specification level. If necessary, they must be specially trained, but they must be of a calibre capable of being trained.

This may seem a formidable task to achieve, but I think that as soon as it is realized by the maintenace authorities that museums must be run as first-class installations, like computer centres or animal laboratories, not just like another office block, then suitable personnel will be made available.

THE ORGANISATION OF MONITORING

All automatic control is initiated by sensors, which are usually devices which measure some variable in the environment, such as RH or illuminance, and convert this measurement into an electrical signal.

There is, or should be, a double sensor system, consisting of (1) control sensors, and (2) monitoring sensors.

Control sensors operate on the system either directly (by causing, say, a valve to close) or indrectly via an electronic processor. Increasingly today signals are processed, thus simplifying mechanical linkages, which are prone to failure, and allowing for some built-in decision-making.

The purpose of the monitoring sensors, which send

their output to a bank of dials and recorders at the control centre, is for us to be able to check that the system is operating correctly, to take a record, and to interfere when necessary.

In many museums and galleries the building itself may not be under the control of the curatorial staff. For example in the London National Gallery responsibility for the paintings is vested in the Trustees, but the building and its maintenance is under the control of the Department of the Environment (e.g. Ministry of Works). In other cases maintenance may be sub-contracted.

Whatever the system, it appears we should make a principal of ensuring that the conservation or curatorial staff is able to check that the climate control is working to specification. This also implies that a member of the conservation/curatorial staff should be designated as climate control officer, with this specific responsibility.

But what good is a climate control officer without instruments and the capability of using them?

THE BASIC MONITORING INSTRUMENTS

<u>The two absolutely essential instruments, without which a museum becomes incapable of operating effectively, are the light meter and the wet-and-dry-bulb hygrometer</u>.

The cost of both these instruments is negligible, even for the poorest museum. Instruction in their use is now given in all reputable training courses for curators and conservators. Indeed one might use this as one criterion of respectability! Two good examples of which I have experience are the Museum Studies course at Leicester University and the courses given to curators and conservators at the Rome Centre.

In spite of this it must be said that probably the majority of museums in the world today are without a single member of staff who can use both instruments reliably.

It is not so easy to go grossly wrong in light measurements provided that one understands the use of the different sensitivity scales and how one should hold the instrument.

The situation is far worse with hygrometers, and worst of all with that very common museum instrument, the recording thermohygrograph. While generally reliable in indicating changes, this instrument slowly drifts out of calibration until the readings may be incorrect by 15% or more. Meanwhile the paper is dutifully changed every week, and the records accumulate in storage - as so much waste-paper.

Yet it is perfectly simple to ensure that these records are reliable and, just as important, to give any future investigator confidence that they are indeed reliable. This is not intended to be a course of instruction on the use of instruments, but it does no harm to be reminded that 8-day recording thermohygrographs should be checked at least every two months with a wet-and-dry-bulb instrument, and that a <u>record</u> of the recalibration should be made on the chart paper.

The wet-and-dry-bulb instrument should be used strictly according to instructions, and the sleeve over the wet bulb should be kept clean by using only distilled water and renewing the sleeve frequently.

WHY ±5%?

Conservators are in a weak position versus engineers in one respect: quantitative evidence on the importance of strict RH control is inadequate. It is easy to demonstrate that a wood panel moves when the RH changes and to measure how much and how fast it moves. It is also easy to show that the paint cracks in response to frequent panel movements, and how detachment begins at the edges of the islands of paint so formed. Furthermore a great number of cases are on record of damage by splitting and warping, nearly always under low RH conditions.

But when an engineer suggests that an RH to ±10% will do as well as ±5% we are hard-pressed for evidence to refute him. All we can say at the moment is that good machinery well-maintained will easily give ±5%, and since such immensely valuable and delicate material is at stake the specification should be ±5% or better. The onus of proof is on those who wish to disprove this assertion.

In fact evidence is hard to obtain. Supposing we took close-up photographic mosaics of 100 panel paintings, then subjected them all to RH cycles of ± 10%, and finally repeated the photography. If the result showed no visible damage from this treatment we would be very little better off for evidence, since the aim is to prevent damage to a single important panel after many years of fluctuation.

DAMAGE THROUGH BADLY MAINTAINED CLIMATE CONTROL

An equipment malfunction can produce an artificial climate quite as dangerous as winter-heating dryness or humid-tropic dampness. Badly maintained air conditioning can do more harm than good. In most cases the harm will not be noticed, and might not indeed be visible, though acting as the seed for future damage.

One solution is to fit override switches, as has been done in a portion of Birmingham Museum and Art Gallery, which close down the whole installation if it runs outside certain limits. For example, with a specification of ±5% we might set the override to ±15%.

Outside the humid tropics, in almost every case less harm would be caused by a complete shut-down than by continuing a malfunction outside these limits until repair is at hand.

The only danger seems to be that under poor maintenance the plant might come to be idle for a major part of the time.

ALTERNATIVES TO FULL AIR CONDITIONING

Because of bad maintenance, expense, and world energy shortage, it seems very desirable to seek for alternatives to the air conditioning of the whole exhibition space.

Systems have been proposed for RH control and air purification, both mechanical and non-mechanical, of individual cases or of a line of such cases. Within the last year Stolow has written an excellent review of some proposals and solutions [1], and the present author has attempted to advance the theory behind the unsealed case containing a buffer [2].

Those members of ICOM Conservation Committee interested in air conditioning and climate control could raise the standard of conservation more effectively than in any other way by improving maintenance of present systems while researching systems of high-quality climate control which:

(1) are of easy maintenance,
(2) are cheap to buy and maintain.
(3) are unobtrusive,
(4) use little energy,
(5) do not restrict the viewing of the exhibits, and
(6) do not endanger security.

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FURTHER STUDIES ON THE INTERNATIONAL BLUE-WOOL STANDARDS FOR EXPOSURE TO LIGHT

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FURTHER STUDIES ON THE INTERNATIONAL BLUE-WOOL STANDARDS FOR EXPOSURE TO LIGHT

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SUMMARY

An instrumental measurement of the changes in reflectance in terms of CIE tristimulus value Y, the luminous reflectance, is employed as an objective measure of the rate of fading of the British Standard BS1006:1971 (ISO R105) blue-wool standards 1 through 5. A tentative relation of the change in Y value (ΔY) with steps in the standard geometric grey scale (BS2662) is noted. In addition, the relative rates of fading of the blue-cloths in a carbon-arc and a xenon-arc fadeometer are reported in terms of the visually-rated geometric grey scale steps; the rates of fading in the xenon-arc fadeometer and under "daylight" fluorescent lamps are reported in terms of instrumentally measured changes in reflectance. Such exposure data are useful for establishing the photochemical stability class of an artist's or conservator's material during accelerated aging tests. One of the principal objectives of this research is to recommend that the blue-wool standards be used as inexpensive monitors for the exposure of materials to light in museum galleries and showcases.

INTRODUCTION

The inherent photochemical stability of the materials is of major concern to museum curators because they must be informed concerning the relative risk of exposing various materials during exhibition. To conservators, the stability of the materials used in restoration and preservation is of basic interest. Both of these concerns about photochemical stability involve not only the direct effect of light but also the effect of temperature, humidity, atmospheric pollutants, etc., acting in combination with light. To this end, a need exists for a simple, objective means by which effective total exposure can be monitored by which materials of the artist and conservator can be classified according to their relative photochemical stability.

The purpose of this report is twofold: (1) to propose a method for monitoring photochemical exposure which is objective, simple, inexpensive and reliable; and (2) to recommend a scheme of classification of photochemical stability based on this method.

BACKGROUND

In the report made at the last triennial meeting (Paper 75/19/4 [(1)], the author proposed three classes of photochemical stability based on British Standard BS1006:1971 [(2)]. (The International Standards Organization's (ISO) Recommendation R105, which we will refer to throughout this report, is the basis for British Standard BS1006:1971, the Swiss SNV 95 8 10 and similar documents issued by individual countries.) These proposed classes are summarized once again in Table 1. The Intended Useful Lifetime in Table 1 is based on exposure on a well-illuminated museum gallery wall at about 150,000 footcandle hours of exposure per year [(1)].

TABLE I

Standards of Photochemical Stability for Materials in Conservation

Class	Classification	Intended Useful Lifetime	Approximate Equivalent Standard of Photochemical Stability
C	Unstable or Fugitive	Less than 20 yrs.	BS1006 Class 3 or Less
B	Intermediate	(20-100 yrs.)	(3 to 6)
A	Excellent	Greater than 100 yrs.	Greater than BS1006 Class 6

The internationally-recognized ISO R105 fading standards consist of eight different blue dyes applied to wool, each dye of which fades at a different rate. The individual dyes were selected so that each one in the series would fade at half the rate of its lower neighbor in the scale starting from the least permanent (most fugitive), No. 1, to the most stable, No. 8. Depending on the individual dye and the specific exposure conditions, this ideal relationship in the rate of fading is not strictly adhered to. Nevertheless, rate of fading as a function of the exposure (intensity multiplied by time) is linear over a wide range of exposure conditions.

The degree of fading of the blue-wool cloths can be reported by comparing them to a standard grey scale such as British Standard BS2662:1961 [(3)]. (Other countries recognize and issue this same grey scale because it is also part of the International Standards Organization's R105.) This standard of comparison consists of five pairs of grey panels in which one half of each pair is the reference, set at a Munsell value of 5. The other pairs each contain chips of grey

that are progressively lighter in the series. Thus the geometric grey scale contrast of panel 4 (GGS4) is equivalent to 1.5 NBS units of color difference, panel 3 (GGS3) has a pair of grey cards that differ by 3.0 NBS units of color difference; GGS2 is equivalent to 6.0 NBS units of color difference and GGS1 to 12 NBS units. To rate the degree of fading, the exposed (faded) blue cloth is compared to unexposed cloth and the degree of contrast (degree of fade) is compared visually with the degree of contrast in one of the four standard contrast steps in the geometric grey scale. Thus a typical degree of fade might be stated as follows: "a given blue-wool standard, after so many hours of exposure under specified conditions, has faded to a geometric grey scale constrast of between 2 and 3 (GGS2-3)". A plot of the grey-scale change vs. the logarithm of the exposure, as shown in Figures 1 and 2, is essentially linear, although the proportionality may require a power function other than 1.0 (in other words, the slope may not be ideally 1).

A convenient form of these ISO standards for museums is the small card available from Schweizerische Normen-Vereinigung [(4)]. One of these was illustrated in a recent publication [(5)]. The card contains rows of the eight standards, each lightly glued adjacent to one another and in order. Each small piece of the standard cloths measures 0.9 x 4.5 cm. The total size of the card is 12 x 4.5 cm., leaving room for labeling and attachment. During exposure, one half of the set of standards is either cut off and set aside for an unexposed "control" or is covered with an opaque material such as aluminum foil; the other half is left exposed to the light. The amount of fading can be periodically evaluated relative to the four-step geometric grey scale.

RATES OF FADING RELATIVE TO GEOMETRIC GREY SCALE

It is frequently useful to be able to compare relative speed of fading or other photochemical changes under different conditions of exposure in a museum showcase, on a gallery wall, or under accelerated-aging conditions. Our last report (75/19/4) presented curves of the rate of fading of blue-wool standards under four different conditions: (a) a north wall in a gallery at about 150,000 footcandle hours per year (about 1.5 million lux hours/year), (b) an RS-type sunlamp, (c) "daylight" fluorescent lamps and (d) under glass on the roof in Pittsburgh facing south. The degree of fading in these curves was visually evaluated by comparison with the Geometric Grey Scale, British Standard BS2662. At this time we wish to report similar curves for exposure in a xenon-arc fadeometer (borosilicate-glass filters) (Figure 2) and in an old model Atlas single-carbon-arc fadeometer ("Sunshine" carbons, Corex D glass) (Figure 1). The xenon-arc machine is an Atlas Electric Devices 600 WRC weatherometer with the samples carried on a drum of 60 cm.-diameter instead of the standard 96 cm. The slopes of these

curves vary from 0.8 to 0.9 for the xenon-arc to 0.7 to 0.8 for the carbon arc.

INCREASED PRECISION IN MEASURING FADING OF BLUE CLOTHS

Admittedly, the precision in visually rating the degree of fading in terms of the grey scale is limited. To increase the precision of such fading curves, an objective instrumental measurement of fading is needed. Several years ago we reported some preliminary results of using spectrophotometric measurements to increase the precision of reporting fading rather than visual comparison with the geometric grey scale [6]. In the past year The Materials Center of Carnegie-Mellon University has completed extensive measurements of the rate of fading of the blue-wool standards using the Small-Area-View (SAV) Color-Eye instrument [6] and the small cards supplied by the Schweizerische Normen-Vereinigung. The SAV Color-Eye is able to measure the reflectance of samples that are only 1/4" in diameter. Typical results are shown in Figures 3 and 4. The curves in Figures 2 and 3 - one based on visual ratings and the other on instrumental - are derived from the same exposed standards. No individual observations are reported in Figure 2 because the extensive numbers of data points are too numerous to be placed in this one diagram; they will be reported in a subsequent publication.

In Figure 4, data are reported in terms of footcandle hours under a bank of "daylight" flourescent lamps in a room maintained at 50% R.H. and at sample temperatures of about 80°F. These data, by Dr. Jonathan Arney of the Center's staff, are based on the reflectance at various wavelengths selected to be close to the point of maximum absorption of the particular blue-wool standard. In 1963 Friele reported similar results in terms of millions of lux hours in the Xenotest apparatus although he simply used the reflectance at 620 for all standards [7].

We have analyzed the results of the xenon-arc exposures (Figure 3) both using the luminous reflectance (Y) and the wavelength of maximum absorption and find equally good correlation either with the Y value or with the reflectance values at the approximate wavelength of maximum absorption, 620 nm, the measurement Friele used. Correlation coefficients of Y values versus exposure (relative intensity multiplied by the time in the xenon-arc fadeometer with borosilicate glass filters) were as follows: 0.994 for blue cloth No. 1 and 0.995 for blue cloth No. 2 (using data only up to geometric grey scale contrast of 1), 0.992 for No. 3, 0.978 for No. 4, 0.974 for No. 5 and 0.973 for No. 6. We are convinced that the use of objectively measured values in terms of Y (which we prefer to use at present), or 620 nm or the wavelength of principal absorption are all more satisfactory to follow the rate of

fading than plots of color difference (ΔE) as has been employed by Berger and Brockes and others (8).

In Figure 4, one can observe that the spacing between the five standards and the steeper slope for standard number 4 when exposed to fluorescent lamps are similar to the behavior under the xenon-arc shown in Figure 3. Data for blue cloth No. 6 are not shown in three of the curves presently reported because its low rate of fading is so slow that insufficient data were available at the time of the preparation of this report.

RELATIONSHIP OF CHANGE IN REFLECTANCE AND GEOMETRIC GREY SCALE CONTRAST

It should be possible to relate a given degree of change in instrumentally measured luminous reflectance or spectral reflectance of the samples to a given visually rated grey scale contrast between faded and unfaded samples. Berger and Brockes determined, for example, the color difference (ΔE) that was related to the geometric grey scale 3 (8). Our initial results, shown in Figure 3, indicate the changes in luminous reflectance (ΔY) that are approximately equivalent to geometric grey scale contrasts 3, 2, and 1. This work will be confirmed more thoroughly through additional experiments. The principal purpose of these initial observations, however, was to show that the plots of the logarithm of time vs. change in reflectance in Figures 3 and 4 was linear throughout the range of visual change in which the blue cloths are normally used -- that is, over a range in grey scale contrast from 4 to 1. The equivalent grey scale changes using the reflectance at the wavelength of maximum absorption in Figure 4 resemble those in Figure 3 but do not occur at precisely the same intervals.

The reason for the marked nonlinearity of the change in Y value at high degrees of fading, seen especially in blue cloths Nos. 1 and 2, is that the dye has almost completely faded at this stage and the wool itself has begun to yellow.

LIMITATIONS TO PRESENT DATA

The importance of the four curves reported in 1975 and two presented now is to demonstrate the principle that such curves can be developed with practice and little expense, simply by visually comparing the degree of fading of the blue-wool standards with the steps on the geometric grey scale, very much as the recommended procedure in the International Standards Organization's R105. The plot

of grey scale change vs. the logarithm of the exposure tends to be linear. ("Exposure" is time multiplied by intensity of illumination, or simply the time if the intensity is practically constant.)

It is recognized that the uncertainty in such visual ratings is considerable, likely to be no better than ±0.5 grey scale units, even if three to five persons rate the degree of fading in terms of the grey scale and an average of their ratings is taken [9]. This degree of uncertainty is indicated in our data for fading on a gallery wall (Figure 1 in Report 75/19/4) [1] and by the scatter of the observations in the present Figure 1. It is for this reason that all of the visually rated curves that the author has reported have been based on the average of at least three separate sets of blue-cloth exposures rated by two observers (Figures 1, 2 and 3 of this present report are based on the average of six separate exposures and the average visual rating by two observers.)

The six sets of visually rated curves and the instrumentally measured curves in Figures 3 and 4 must be regarded as preliminary findings, giving only approximate rates of fading. Much more work will have to be done to determine the variations that will be encountered when different investigators attempt to duplicate the measurements under similar but obviously not identical conditions of exposure.

CONCLUSION

The author's purpose in reporting the sets of fading curves under six different exposure conditions has been first of all to demonstrate the principle of how to obtain such plots and, secondly, to establish an initial set of curves in which the relative rates of fading of the blue-wool standards under various exposure conditions can be further studied and compared. These preliminary measurements, for example, have provided us with initial estimates of how long it would take for accelerated aging tests to determine if a material is in class C or class A of the proposed standards of photochemical stability (Table I).

Another potential use of these standards is as an inexpensive and unobtrusive monitor for exposure. Light intensity on museum walls and showcases usually varies with the time of day and season of the year. In a sense, the blue-wool standards "integrate" the varying intensity, providing an indication of the net amount of exposure (intensity vs. time, along with a certain influence of temperature and humidity). Thus, if we determine their rates of fading - that is, the slope of the curves - then by observation of the rate of fading of the most fugitive standards, we can predict how long it will take to accumulate a given number of lux hours (shall we say) in a particular location. For example, we

know that alizarin tints are equivalent to BS1006:1971 standards 4-5 on light fastness, and gamboge washes are equivalent to standard cloths 2-3 [10]. Many natural dyes on textiles fade at a rate equivalent to BS1006 blue cloths 2 and 3 [11]. Thus, after brief exposure of a set of the blue cloths in a given location in a museum, and observation of the degree of fading of standards 1 or 2, one can predict with some assurance how long it would take materials equivalent to standards 3 and 4, such as alizarin or gamboge, to fade in the same location either to a geometric grey scale contrast of 4 (GGS4, just perceptible difference) or to a more severe degree of fading such as GGS3, 2 or 1.

Additional measurements will be carried out in the future to increase the precision and reliability of these initial findings. We intend to repeat the measurements many times over in the coming three-year period, using spectrophotometric measurements to increase the precision in which the rates of fading can be followed [12].

ACKNOWLEDGEMENT

The data in Figures 1, 2 and 3 were obtained by Mrs. R. A. Curran, who also determined the correlation coefficients and slopes for the curves.

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11. T. Padfield and S. Landi, "The Light Fastness of the Natural Dyes," Studies in Conservation 11, (1966) 181-193.

12. Friele recommends the use of $\Delta R/R$ at 620 nm instead of ΔY or ΔR. Full consideration will be given to his views in this matter.

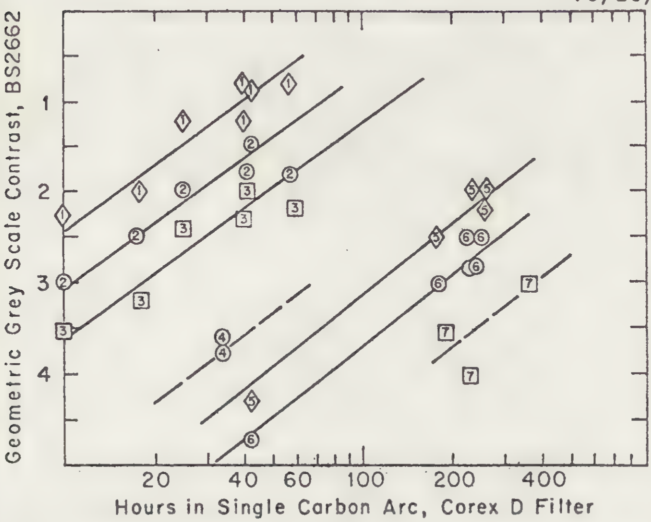

Fig. 1
Fading of BS1006: 1971 Blue Wool Standards in Fadeometer

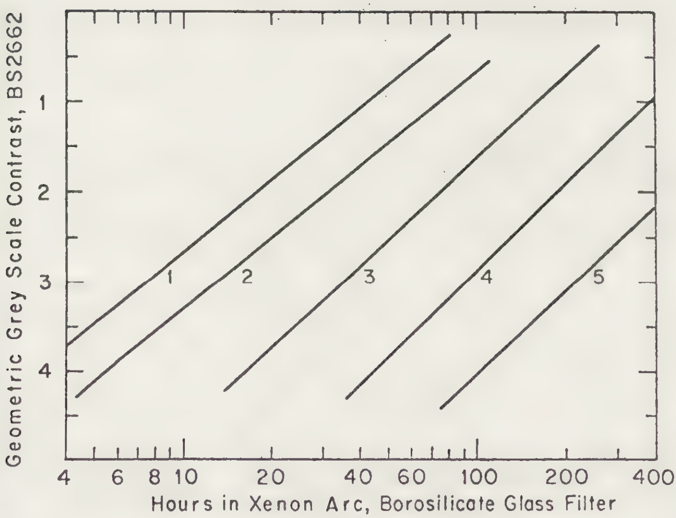

Fig. 2
Fading of BS1006: 1971 Blue Wool Standards in Fadeometer

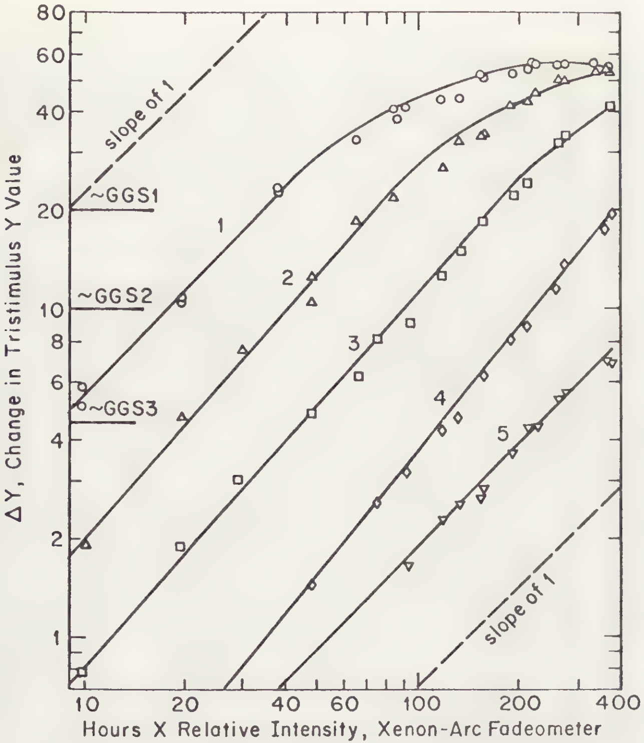

Fig. 3
Fading of BS1006:1971 Blue Wool Standards 1 to 5 in Xenon-Arc Fadeometer, Borosilicate-Glass Filter.

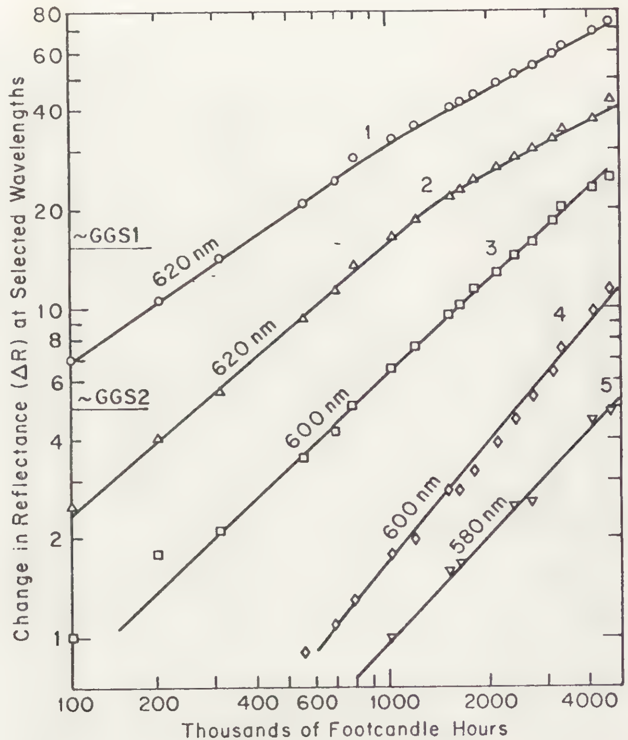

Fig. 4
Fading of BS1006:1971 Blue Wool Standards 1 to 5 Under "Daylight" Fluorescent Lamps

78/18/3

NBN L 15-151: A BELGIAN STANDARD ON MUSEUM LIGHTING

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NBN L 15-151: A BELGIAN STANDARD ON MUSEUM LIGHTING

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SUMMARY

To realize a good museum lighting, curators need a wide theoretical and technical knowledge. In order to be of some help in this matter, the BNCV is working on a Standard for Museum Lighting. Most of the problems, a curator has to deal with, will be discussed and illustrated with examples. Detailed and practical information on trade names, suppliers and prices can be obtained from the "Koninklijk Instituut voor het Kunstpatrimonium". The standard will be available in the course of 1979.

Nowadays, almost every curator is well aware of the importance of a good museum lighting. The lighting levels of 50, 150 and 300 lux, as proposed by G. Thomson (1) are therefore widely accepted all over the world. There are also many publications available on the damaging effect of IR and UV radiation and on the possibilities to eliminate those harmful rays. Despite all this information, we know from literature (2,3) and from our own experience, that the accepted standards are not al ways respected. One of the reasons is that a good museum lighting, respecting the standards and taking precautions against all harmful radiations, is not easy to establish. The theoretical data have to be put into practice and this involves problems such as :

- where can one buy some filters or lamps in one's own country
- what is the effectiveness of new filters
- what about fluorescent tubes or other lamps, which have not been registered yet in recent publications.

Manufacturers are not always aware of, or interested in, the specific problems of museum lighting and therefore, commercial arguments are very often used in stead of scientific ones. As we can see, a good museum lighting is a complex problem which can only be solved by curators, spending a great deal of their time on studying recent literature.
Therefore, in 1972, the BNCV (Belgisch Nationaal Comité voor Verlichtingskunde) decide to enact a Belgian Standard on the subject. A committee, consisting of a wide spectrum of disciplines (lighting specialists, electricians, curators, restorers, oculists, scientists, representatives of the lighting industry) was appointed.
Using some basic literature on museum lighting (4, 5, 6), a text was drafted, combining theoretical and practical information. At the end of this publication the content of the Belgian Standard is given.
After a short historical survey of the lighting equipment and the successive fashions in lighting, a scientific description is given of : photometric and energetic units and how to measure UV, visible and IR radiation. Special attention is called to the deterioration factor of lamps, the influence of natural and artificial lighting on works of art is also compared. In the chapter on preservation conditions, the lighting levels, the elimenation of UV and IR radiation, the exposure-time and the climatologic conditions are discussed.

This is followed by detailed information on colour rendering ; reflection problems; general and local lighting Several examples are given of good showcases, each with the best lighting installation. Finally, the lighting of libraries, restoration worshops, reserve rooms, museum entrances and -staircases, and the maintenance of the lighting installations is discussed.

As it is not allowed to mention any commercial name in an official standard, the technical characteristics of a series of lamps, filters and measuring apparatuses are given. For more detailed information (trade names, suppliers, prices) the KIKP (Koninklijk Instituut voor het Kunstpatrimonium) can be consulted.
A bilingual edition (Dutch-French) of the standard will be available at the "Belgisch Instituut voor Normalisatie", (Brabançonnelaan 29, B-1040 Brussel, Belgium) in the course of 1979.

NBN L13-151 : Lighting of works of art and collection objects.

Introduction

1. Generalities

2. Basic considerations

Photometric units in connection with the visual perception of the objects ; energetic units in connection with conservation conditions and the protection of works of art ; relation between luminous and energetic units ; measuring of energetic radiation, luminous radiation and UV radiation ; problems in lighting works of art ; preservaton of work of art.

3. Deterioration factor

Influence of light on works of art ; natural and artificial light : quantitative and qualitative effect.

4. Preservation conditions :

Protection against IR and UV ; light sources; lighting levels ; exposure time ; sensitivity of works of art to radiation climatologic conditions.

5. Installations

Repartition of luminance ; colour rendering ; reflection factors ; general lighting.

6. Luminous constructions

Natural and artificial lighting ; position of light sources ; colour temperature.

7. Equipment

Show cases, partitions, walls

8. Permanent and temporary galleries

9. Lighting of auxiliary places

10. Maintenance of lighting installations

Literature

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78/18/4

SOME TOOLS FOR THE LENDERS AND BORROWERS OF HUMIDITY-SENSITIVE OBJECTS

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SOME TOOLS FOR THE LENDERS AND BORROWERS OF HUMIDITY-SENSITIVE OBJECTS

R.M. Organ

Potential borrowers of objects need to learn the conditions of relative humidity and temperature to which the objects have been exposed during the previous year. The briefest description of the conditions contains only three figures - maximum, minimum, and mode - for RH and T. This paper describes practical methods of examining fifty-two hygrothermograph charts in order to discover the modal value: by inspection; by measurement using map-measurers, scales, a cylindrical lens and scale; by superimposition of transparent copies of the charts. The advantages and disadvantages of the various methods are considered in terms of the work they involve and how they provide onformation for a single document that will be accurate and will inspire confidence in its recipient

Responsible people have become concerned in recent years about the risk of damage to cultural objects while lent for display to an Institution located in a different climatic zone from that of the owner. There would, however, be no need for concern if such an object could be maintained constantly, both during travel and at the borrowing Institution, in the conditions to which it had become acclimatised. Technically, any reasonable values of relative humidity can be maintained for limited periods. In order to achieve the correct values, the borrower needs to obtain from the lender a document which defines the climate to which the object has been accustomed. The owner about to make a loan may also reasonably require of the potential borrower a statement of the conditions to which the object will be exposed. The data can eb expressed most simply as the extreme values and the most common (modal) value of both relative humidity and temperature surrounding the object for the previous twelve months. The full cycle of the seasons is needed because it is to these that th object has become habituated.

Anyone who has sought to wrest from a file of hygrothermograph charts data that can be put into few words will recognise the practical difficulties in so doing. As an example, an actual statement about a relatively well controlled area reads as follows: "In general, these charts show relative humidity readings for entire weeks lying within the acceptable band. For twenty-four hour periods they may vary only within two

per cent. There are, however, isolated changes of 2 to 6 per cent, from 1 to 24 hours in duration, that occur from one to four times in some but not all weeks Exceptionally, a change amounts to 10 to 14 per cent during four weeks in the September-October period. One 20 per cent spike of one hour duration may have been very bad for particular paintings."

A full cycle of the seasons contains fifty-two weeks. To look through fifty-two charts and to tabulate the maximum and minimum excursions of the traces for each week, preparatory to selecting their maximum and minimum values for the entire year, merely requires persev erance. Estimation of the most common value is, however, much more difficult. The following account presents several methods of determining and of presenting the required facts.

Tool #1 Simple Inspection
This procedure is practicable if the environment is very well controlled, so that: all traces on the chart are substantially straight and level; or if any changes are offesets of limited duration, even perhaps recuuring regularly at intervals of twenty-four hours. Then inspection may reveal a most common value for the week. This ought to be the value for which the humidistats and thermostats have been set.

Some charts may be found to contain so many irregularities that there is no single horizontal trace, even interrupted, that has sufficient duration to be considered the most common value. In this event we may have to use instead an average, hoping that the object has been able to survive the regular stresses that will have afflicted it. An average may be found by laying a thin straight line on the trace and then changing its slope and position until as much of the trace appears to lie above the line as lies below it. Then a point at the middle of the straight line may be taken to represent the average value.

1a A thin straight line may be formed for this purpose by a 450mm length of very fine black thread, pulled taut between the fingers and laid close against the chart.

1b Holding the thread can be made easier by tying each end of it to a 30mm (1 1/8") "curtain ring"

1c Even better, a flat "U-shape, 300mm (12") wide, may be made from springy wire and the thread glued between its short arms under tension. Suitable bending of the base of the "U" will provide loops that can serve as handles, making movement of the thread over the chart very convenient.

1d Another practical embodiment of a thin straight line may be made by scratching a fine line on a piece of transparent plastics sheet or along the centre-space of a clear plastics "dime-store" ruler, on a face that can be laid in contact with the chart, then filling it with black pastewax or black water-proof drawing ink. The edge of a ruler will not do: the eye will only balance areas above and below the straight line if there are no inequalities in the two fields of view.

When using the inspection method, the three figures, maximum, mode, and minimum, are written down for each week of the year in tabular form and then inspected again. The summary column will be assigned the highest maximum and the lowest minimum. The mode will be that modal value that appears most frequently

An Institution to which such a report is sent will be as interested in the figures for the separate weeks as in the summary. From these it may be possible to select the most suitable season of the year for a particular object that is to be lent.

Inspection is a rapid procedure, occupying only about one minute for each chart.

Tool #2 Measurement
Visual estimation is quick, but the receiver of the document must have confidence in the estimator. Methods involving measurments which can be quoted usually inspire more confidence. The problem then in estimating the most common value becomes one of measuring how many hours during the entire year the object has spent in air having each value of RH and T. Taking the charts for each week in turn, it is necessary to total the hours that the trace has occupied at, say, 55%, then at 54%, etc: in one week most of the time might have been spent at 55% and a little time at 50% whereas in the next week the reverse may have been true. The summation for the year can take account of such variations.

2a The Map-Measurer
This device appears in two forms. The least-sophisticated has a small knurled-edge disc whose centre-hub is threaded and runs on a threaded rod about 20mm long whose ends are secured in the two short sides of a flat stirrup. The stirrup is in turn mounted on the end of a rod that serves as a handle. The device is intended to measure the length of a winding road shown on a map. It is used by first spinning the disc so that it moves along its threaded rod until it stops at the end. The edge of the disc is then placed on the line to be followed, at its beginning, and the device

is wheeled along that line, the disc rotating as it goes, until it is lifted off at the end. by now the disc has rotated itself along the thread. In order to discover the length of the line travelled the process is reversed by placing the edge of the disc on the zero of the scale on the map and wheeling it back to its original position. The distance now traversed along the straight scale equals the distance earlier wheeled along a winding line. The same device can be used to add successive lengths of line by wheeling it along each in turn without returning the disc to zero in between.

A more sophisticated pattern of map-measurer has a large dial with pointer geared to a small wheel but it can be used as suggested above, ignoring the graduations on the dial, which will not be appropriate to this present procedure.

In order to total up the durations of each level of relative humidity or temperature on the chart of a hygrothermograph the entire length of a trace must first be divided up into so many hours at, say, 52%, so many at 50%, and so on. This may be done visually by making pencil marks at the beginning and end of each "dwell". Any steep rises or falls should be left out of this process, only dwells at one level, of duration greater than one hour, being marked off. Next, lay a straight-edge above the highest level to be measured, zero the map-measurer, and roll it along the level between each pair of pencil marks. Finally, roll it back along the time scale on the same chart in order to discover the total number of hours at this value of RH. Write this down and repeat the process for the next level of RH, two units lower. Repetition only one unit lower is difficult, because the disc has a thickness little less than the spacings between the RH lines on the chart. Another difficulty arises using the simple device because its body moves towards the viewer as the disc rolls and this tends to obscure the pencil lines. For this reason the pencil marks must be long. They should also follow the curvature of the time lines on the chart.

The result of this exercise will be a table showing hours of duration at each even-numbered (or odd-numbered, according to choice) value of RH and T for one week. If now the number of hours is totalled it should amount to 168 (7 days of 24 hours). In practice it will not, because either the instrument was left to run too long or started unusually late in the week, or because there have been many sharp changes which it has been impracticable to measure. In order to allow comparison of performance of the climate-control equipment from week to week it would be useful to

smooth out these irregularities of measurement. The methematical device of conversion to percentage will serve: divide each duration into the toatal of hours and multiply by 100. The result will be a table of percent of total duration spent at each level of RH & T.

R H %	Duration h	Fraction of measured h	per cent of measured h
56	15	15/98	15,3
54	9	9/98	9,2
48	18	18/98	18,4
46	-	-	-
44	-	-	-
42	28	28/98	28,5
40	-	-	-
38	-	-	-
36	-	-	-
34	14	14/98	14,3
32	14	14/98	14,3
	98		100,0

Table 1. Data from chart 4023, 12/18/77

Repetition of the procedure for all weeks will result in 52 tables. Summing the percents at each level will give totals for each level. The largest of these will be the most common level.

The principal disadvantages of this method of measurement are that the device obstructs viewing of the trace unless the sophisticated pattern is used and that a very irregular trace makes the procedure tedious to the point of frustration, as much as thirty minutes being required for mesurement of each chart. Nevertheless, it is useful when there are cyclic changes because the duration at each level is summed automatically, without tedious writing and adding.

2b Scaling

A simpler way of obtaining the total dwell at each level is to measure each dwell against a supplementary scale, write it down, and then add the series. The scale can be made by cutting a seven-day long strip from an unused chart, cutting off the days and numbers so that each printed time-division line terminates at the cut edge of the paper, then renumbering the lines from zero by two hours, emphasising the tens, to 160. After some practice it will be found that a shorter length, perhaps only 100 hours, will serve. This scale

snould not be varnished or protected in some manner because, left as it is it will expand or contract with ambient changes and will always match the charts being measured. It is used by setting its zero against the beginning of a dwell and reading off the number of hours level with the end of the dwell. Speed comes with the ability to place the scale with the left hand while writing down the reading with the right hand. A pocket calculator can help with the arithmetic. Better, one that prints the numbers that have been entered.

This method generates much less frustration then the map-measurer but it highlights the uncertainties of deciding during the preliminary pencil marking exactly when a trace has departed from one level and has moved to the next. For practical purposes, it is adequate to choose levels 2% apart, since the instrument is only capable of an accuracy of 3%.

2c Rod and Scale

If some approximation in RH level is allowable, then there is an optical method of isolating for attention all traces that lie within a narrow band. In principle it consists in placing a glass rod, acting as a cylindrical lens, along the 290mm length of a particular RH level. Then any portion of the trace which lies at and somewhat above and below this level will be visible, its thickness much magnified, within the rod. Laying the scale alongside enables the duration of each dwell to be read off.

R H %	Durations h		Total h	percent of 164h
39-41	3+9+20+6+12+5+4+13+19	=	91	55,5
37-39	3+33+7+13+6+1+10	=	73	44,5
			164	100,0

Table 2. Data from chart 4023, 1/9/78

Some practical details follow. For the usual chart, in which 100% of RH occupies 40mm (1,58") a 3mm diameter glass rod will present to view almost all of a single space (0,8mm) representing 2%. A trace about 0,4mm wide will hten have an image occupying about half the width of the rod. It is convenient to lay the glass rod along a printed line so that the image appears exactly in the centre. This is easy to do with great precision and corrects for variable position of the viewer's head. Difficulties only arise if the chart has been creased or folded: it must be flat.

Identification of the line being viewed needs a little practice. The printed figures (30, 40, 50, . .) can be seen clearly and when the rod has been rolled to the next position, enough of the figure can still be seen for identification. For the next three positions memory will serve; or one can look at the printed line, not magnified, just outside the end of the rod; or, with a sharp pencil, tiny squat numerals 2, 4, 6, 8, can be drawn across the printed lines in clear areas of chart so that they appear magnified between 40 and 50 or wherever needed.

Visibility is best if light comes from the end of the rod, not from its side.

The glass rod can be ground off at its ends to protect the user from sharp edges but it should not be fire-polished because an over-enthusiastic torch-man may create thickened ends that will prevent the rod from lying in contact with the paper. The rod is also somewhat flexible. Although it can be managed perfectly well with two hands, the fingers that press it into contact with the chart will onscure parts of the image. It is convenient to confine it beneath an inexpensive dime-store transparent plastics ruler, filing notches in its stiffener-ribs to allow the rod to be located along its centre. An engineer's twist-drill of diameter slightly greater than the 3mm will notch a polystyrene rib very cleanly if slid to and fro, not rotated.

There is no need to pencil-mark the trace when using a rod, this saving about eight minutes work. Whenever the trace rises or falls sharply the image will be found to be thin and sloping across the rod. These may be neglected if the percentage method of calculation is employed. When using a 3mm rod there is a very slight overlap between adjacent positions, the same length of trace appearing twice, once fully and once thinly at the edge of the rod. The same length should not be measured twice. A rod about 2,8mm would be better if available.

The time needed to record an entire chart in full detail is about twenty minutes per trace on average.

2d Rod and Scale, short method
In order to save time the rod may be rolled down, parallel to the chart lines, until a trace is found that has a duration of, say, 14 hours. The actual duration of all such longer dwells is tabulated against the corresponding value of RH. The total time needed for all 52 charts will then be about 17 uninterrupted hours.

Tool #3
All of the above procedures have as their object the condensation of the full data in the charts into easily digestible form. The final statement might be simply the maximum, mode, and minimum values for an entire year: just three figures. No Institution is likely to be satisfied with such a bare statement, however, except in the very first exchanges of ideas. A reasonable presentation of the data would include the three summary figures for each week of the year. This would not only generate confidence in the supplier of the data but would also help the lending Institution to choose the most suitable time of year for the loan of a particular sensitive object. Ideally, the numerical summary should be supported with copies of all of the charts, so that spot checks on the accuracy of the figures could be made and so that the presence of peaks or other rapid changes could be noted. A method of displaying and condensing all the data in one document will now be described.

In principle, each weekly hygrothermograph chart for the year is copied on a transparency and the 52 transparencies are stacked up in register. A final sheet of draftsman's tracing tissue is added and the pack is illuminated from beneath by, for example, sunlight. Then all of the traces can be seen at one time as shadows superimposed upon each other. From a well-regulated environment will come a narrow black bundle of lines which straddles the modal value, together with a few outlying traces. From a poorly-regulated area will come a rather wide band, perhaps twenty or thirty percents wide, made up of clearly separated traces, with a few more outlying even this. Inspection may suggest that there is no common value. Details of the procedure follow.

Copying of the hygrothermograph charts may be done on an office electrostatic copier* supplied with transparent foil+ instead of paper. The best copies will come

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*for example, IBM Copier II. There may be initial difficulties with the cut-off knife.
+for example, Nashua Transparent Projection Film, IF20, Clear

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from machines intended to make copies for use on school overhead-projectors. The copier should be adjusted to minimise greyness of the background. The trace to be copied should be dense and unsmudged: if the pens were running out of ink the line may be too slight to yield a copy.

The stacking of transparencies in exact register requires care. A satisfactory way is to lay them in turn

on a plate of glass raised about 15mm (5/8") by two long strips of wood above the top of a light-box. The separation allows space for fingers and spring-clips. The glass must be about 20 to 24mm shorter than the length of the transparency and may be 20mm wider. Having laid down two films in register above the illuminated glass they are fixed together with spring clips ("binder paper clips", "Bulldog clips") about 8mm deep in the throat. A third transparency is then laid down in approximate register, adjusted to accurate register at the left-hand end, and held down against the glass by finger pressure while the left-hand clip is relaxed, removed from the two transparencies and replaced to secure the three. The right-hand end is then corrected into exact register, the transparencies again held down by finger pressure and the right-hand clip removed from two and replaced to hold three. The small correction at the right-hand end will have set up small stresses in the sandwich of foils but this will be relaxed when the fourth tranparency is added and the left-hand clip is removed from the three and replaced to hold four. This procedure appears to be satisfactory provided that the spring clips are allowed to hang free; provided that they are not so heavy as to bend the foils; provided that the eye is placed always to look down perpendicularly on the work. If the light-box in use is insufficiently bright to allow clear vision through 52 foils then they may be registered in groups of 26 or fewer and combined later. Together they may reduce by a factor of sixty the light transmitted.

After the fifty-second transparency a sheet of tracing foil and then a second glass plate, edentical with the first, are added. These reduce the light intensity by a further factor of twelve. Transparent areas on the two long sides of the charts can be masked off with long strips of aluminum 'cooking foil' incorporated into the sandwich, which is then held together with larger spring clips, at least 19mm deep in the throat, positioned so as to squeeze the glass against the foils, not where the glasses are unsupported by foils.

The light-box used for registratinn can conveniently be the same as that used for viewing: it must be bright Since the bottom transparency is about 4mm below the top one, the traces to be compared are not in the same plane and the usual kind of diffuser-top box will give unsharp shadows of the lowest traces. Failing bright sunlight which can be directed upwards by a mirror, an illumination of reasonably good quality, though not of brilliance, can be obtained from a 40watt pearl lamp placed about 450mm below the sandwich. The shadow of a bottom trace is then widened by about 0,5mm.

Improved quality of shadow and about four times brighter illumination can be obtained by locating a Fresnel lens*

*for example, Edmund Scientific, 10½" square, 5" focus

immediately below the sandwich and placing a 12volt 24watt auto lamp (or 21watt 12volt High-intensity lamp) about 180mm below, with its short line-filament arranged parallel to the traces. The lens should be placed with its correct side towards the lamp: if not, only about half of the chart area will be illuminated. This illumination is similar to that provided for its tranparencies by the illuminated base of an overhead projector, which would probably do quite well.

Copying the foils and stacking them together in register need occupy only a few hours when suitable apparatus is at hand. Visual examination of the sandwich allows the three summary figures to be obtained easily. Much more information than this minimum and in a confidence-inspiring form can be transmitted by making a single photograph: a 35mm slide required an exposure of 30secs at f16 on film of ASA64. Contact printing at full size should be possible using bromide paper. Such a photograph gives an excellent representation of the conditions actually prevailing, showing whether the maximums and minimums refer to occasional peaks of RH and T outside some particular narrow bands representing the usual (most frequent) conditions, or whether the conditions vary rapidly up and down within a wide band so that in fact there is no well-defined 'most-frequent' condition.

If a potential lender in future should receive a document of this second type from an Institution requesting a loan then he may do his duty to the object in either of two ways. He may simply refuse to lend. Alternatively, he may insist upon the use of display cases designed to stabilise the local environment and he may then delay the loan until he has received documentary proof that the cases are indeed working satisfactorily. The documentary proof can be produced by one of the tools and its variants described above, selected to match to the preactical need those skills and the man-hours available. These tools are not sophisticated. Ultimately it is to be expected that the hygrometers now being installed in some museum buildings and connected to a central office for alarm purposes could have their readings sampled at half-hour intervals and recorded both for display and for condensation as above by means of a computer program - quite painlessly, perhaps.

78/18/5

THE AIR CONDITIONING AND SECURITY SYSTEM OF EL GRECO'S 'BURIAL OF THE COUNT OF ORGAZ' IN THE CHURCH OF SANTO TOME, TOLEDO

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ABSTRACT

Measures of the Relative Humidity and temperature was made during six months, in order to know the room climatic conditions.
For to check up the air conditioning system, further observations was made.
The modifications of the room of the picture, the lighting and security systems, was described.

INTRODUCTION

The fact that a picture painted to commemorate a miracle and with a wholly religious purpose should come to be one of the chief examples of 16th century Spanish painting, with universal fame, is an undisputable question which has to be faced. This circumstance has caused some problems of conservation for the picture and of occupation for the Church of Santo Tomé.
The constant passing of visitors in groups of some fifty people supposes some climatic changes that are dangerous for its conservation.
In the decade of the fifties central heating was installed in the Church, which helped to modify the microclimate of the atmosphere in which the picture was sited.
These studies have been made, therefore, with the idea of establishing the climatic conditions in which the picture has been during its existence and testing the efficiency of the equipment that has been installed.
The data obtained may be considered as a homogeneous sample of the climate of Toledo. In the month of April temperatures were low, the heating was lit for some hours in the Church and the month it rained some days. May and June were exceptionally rainy and in the rest of the months measured the climate was dry and warm.

CONTROL OF THE DATA

Two thermohygrometers[1] were installed:one by the picture (Nº1) and the other in the place which, after the work was finished, would be the visitors' bay (Nº2).

The plans of figure 1 show the picture's old position and the alterations that have been made to adopt the premises to the new position.
These data for six months, from April through September, give us an idea of the climatic conditions that the picture has had to stand during its existence and we have used them as a basis for establishing the average values of relative humidity in - which it must remain.
Toledo is right on the meseta of Castile and its climate is - pretty dry, even in winter. It would therefore be counterproductive to submit the picture to an R.H. different from its own average R.H.
The higrometric charts obtained weekly were read taking the - data from hour to hour; we thus know the number of hours it has remained at a particular R.H. or temperature [2]. These data have been grouped by months, and give a fairly good and easily analysable picture of the microclimate of the picture.
Having drawn up the frequency tables (Fig.2) we proceeded to - make a statistical study to interpret the values obtained qualitatively and quantitatively. For this we prepared the histograms of frequencies for monthly periods and setting the R.H. against the temperature (Fig. 3 and following).
The monthly and general averages have been calculated[3]. To find the dispersions of the values with respect to the central value the standard deviation was calculated[4].

TEMPERATURE

Tables 1 (Fig.2) contain the readings of the temperatures and their distribution throughout six months. Each month has two - columns, one corresponding to the site of the picture and the other to the visitors' bay. The data for the two sites agree - pretty well. In the six months studied the maxima came to 35ºC and the minima to 8ºC, taking into account that no data were taken in the winter season. This means that the influence of - the outside climate is very great inside the church.
The average value of the monthly temperatures goes from 17.5ºC to 30.5ºC with an average of 23.9ºC and the standard deviations from 0.97 to 3.83 with an average of 2.
The last column shows the values after the installation of air-conditioning. The temperatures stay close to 20ºC, with standard deviations of 0.64 and 0.90.
These deviations are less than the errors admitted in the measuring apparatus, so we cannot say precisely whether the variations of temperature are real or due to errors of recording and reading. Since then the temperature has remained practically -

constant, uninfluenced by the outside climate or the arrival - of visitors to see the picture.

RELATIVE HUMIDITY

Table 2 contains the numerical data taken from the graphs of the relative humidity during the six months mentioned above. The R.H. varies between a maximum of 80% and a minimum of 15%. The values for the visitors' bay (N) and the site of the picture (C) are similar. The monthly averages fluctuate from -- 32.8% to 56.7%, with some standard deviations that go from -- 4.39 to 11.65.
It sould be mentioned that the standard deviations of the picture site are always somewhat less than in the visitors' bay, as this helps to mitigate the climatic changes outside.
We also observe a decrease in the standard deviation from the first measurements to the last ones, due to the fact that these last measurements were made during the work on the air-conditioning and in the last months the glass had already been placed to screen the atrium, which prevented the circulation of an enormous mass of air with the exterior.In this way a natural protection against climatic changes was created, which considerably diminishes the influence of the outside climate on the microclimate in which the picture and its surroundings are situated.
At the same time there is a saving of energy in the air-conditioning installations which have to work less when the fluctuations of R.H. and temperature decrease.
There follow the values of the Relative Humidity once the air-conditioning system is working. The values stay close together and the standard deviations decrease to really low values, of the order of the errors of the measuring apparatus which, as we have said, vary from ±3% to ±5% according to the class of the measurement. This means that we have moved from a regime of completely uncontrolled R.H., with enormous fluctuations, to a uniform system without changes.
The average R.H. with air-conditioning is 47.8% in the picture site and 44.9% in the visitors' bay and an average of 46.4% with standard deviation of 3.71, as against an average for the period measured of 44.6% and a standard deviation of 7.52.
The choice of the R.H. to which the picture was to be submitted was made in function of the real average R.H. it had had during its existence, for raising the R.H. levels to higher figures would mean a brusque modification of the conditions which the picture had endured, and therefore a risk by breaking the equilibrium already established with the surrounding medium.

The R.H. values recommended[5] when there is air-conditioning are maintained with very wide limits: the maximum was fixed at 65% and the minimum at 40%, for the important thing is to fix the value chosen[6] and decrease to a minimum the fluctuations, which should not be greater than ±3 per cent[7].
The value calculated of the standard deviation is very important, for it is less than the error of the measuring apparatus, ±3%, and than the fluctuations permitted in the R.H.[8].
For greater clarity the numerical data are represented by graphs (Figs. 3, 4 and 5), in order to provide a view of the whole subject. They have been put in the same order as the numbers , plotting R.H. against temperature[9]. The average of all the data obtained that appear in the Summary of Data in Fig. 6 is shown by a dotted line. In this way we see the sinusoid that has been formed during the months of measurement both in the R.H. and in the temperature.
The Histogram of Relative Humidity Frequencies makes quite clear the conditions to which the "Burial of the Conde de Orgaz" has been submitted; these measurements are of great interest, for they calibrate the comfort of works of art, not according to the norm of measurement of habitability but by means of adequate technical equipment[10]. That a work of art may have always remained in the same place is no guarantee of its conservation, and if this place does not have ideal conditions the picture will be submitted to a more or less serious process of deterioration. In our case the damage that the picture presents can be perfectly appreciated in the radiophotograph.
We observe in the Histogram of R.H. Frequencies how from the month of July there is a regrouping of the frequency, due to the installation in the outer atrium of the glass which has helped to form an effective barrier against climatic changes.
The Histograms of R.H. and temperature Frequencies with the air-conditioning working (Fig.6) show us a regrouping in the number of hours it remains with R.H. and temperature constant.
The variation of the R.H. in the visitors' bay is greater than in the picture site owing to the contribution of humidity and temperature made by the human mass of visitors.

AIR-CONDITIONING OF THE PREMISES

The conditions of the premises have been substantially modified in order to create the most suitable atmosphere for the conservation and exhibition of the picture.
In the plans in figure 1 we see the old and new positions; the picture no longer looks towards the Church but towards the bay which is going to hold the spectators.The communication of the

picture room with the Church has been closed with opaque glass so that worship is not disturbed although incommunication is not complete, as the picture is still inside the Church. The separation between the visitors' bay and the picture is a simple iron railing about 1 m. high,which forms a physical barrier sufficient to prevent people going too near the picture. The visitors enter by the steps in the atrium and then along a passage to the bay; they go out by a different door to the the atrium where the visit ends.
To obtain a space as closed as possible so as to insulate it from the climate outside, the three semicircular arches of the atrium were glassed in (~~Fig. 7~~). This was done by means of large panels of glass with swing-doors for people to go in and out. In this way we manage to insulate the precinct effectively and lessen any influence of the climate outside.
The air-conditioning equipment is installed in part of the church choir, making use of the windows in it for the admission and expulsion of air to the exterior.
The control switchboard is in the same place, which has direct acces from the parish priest's house.
The conditioned air circulates on a laminar system, and the outlets in the picture site have been placed in the roof over the railing that separates the public. A curtain of air is thus obtained which insulates still more any outside influence on the climate. The efficacy of this protective barrier is seen very clearly in the standard deviations of conditioned air in tables 1 and 2. The temperature has 0.64 in the picture, as against a standard deviation of 0.90 in the visitors' bay, and the R.H. has 3.38 by the picture as against 4.03 in the bay.In the Histograms of Frequency with air-conditioning there is also a greater grouping of data by the picture than in the visitors' bay.

LIGHTING

We had to obtain an agreeable atmosphere which would at the same time centre attention on the picture alone, but with a limitation of luminosity on the surface of the paint[11],which we have fixed at 150 lux, for although it is impossible to eliminate damage completely[12], the lowest possible levels have been established, as proposed internationally.
The bay is lit by a light placed on the cornice of the vault of the visitors' bay which gives a pleasant degree of vision,but is very weak in comparison with the lighting of the picture, so that the effect is to concentrate all our attention on the picture,giving a sensation of high luminosity.

We also studied the type of lamps to be used in order that the colour should glow as much as possible[13];we chose-halogen-quartz lamps with a colour temperature of 3,200ºK, which provide a warm light that is very pleasing to the spectator. These lamps are provide with ultraviolet filters to eliminate the slight radiation they emit of these wavelenghts.
Two focal points of light were sufficient to obtain a homogeneous illumination, and these are provide with shades to limit the field of illumination and thus distribute the light better. They are placed in the front corners of the exhibition bay (Fig.1), and remain out of sight of the public, concealed by the pillars of the Church.

SECURITY SYSTEMS

Besides the air-conditioning and lighting work, a system of security, control and vigilance has been installed.
Different sets of equipment have been installed according to the areas to be protected, in accordance with the requirements of the places affected.
The doors giving acces to the precinct have been protected with magnetic contacts;an alteration of their magnetic field closes the loop of an alarm.
Direct acces to the picture, through the low railing which separates the visitors' bay from the picture site, is protected by a double equipment of infra-reds with mirror, which operates when the modulated infra-red ray is intercepted which goes from the transmitter to the receiver.
The glass and wall behind the picture are protected by means of vibration contacts, sensitive to mechanical vibrations of the surface protected.
The cupolas of the premises are protected by ultrasonic equipment, which detects the displacement of any intruder in motion.
The electric terminals go to two different points, and the power feed of this equipment is double to prevent possible failures[14].

NOTES

[1]Thermohygrographs of hair and metal couple with weekly record cards. Average accuracy: between 25% and 98% of R.H. ±3%.Below 25% of R.H. ±5%. Between -10ºC and 30ºC ±0.3ºC. In extreme temperatures ±5ºC. In each change of cards they have been recalibrated with a high precision aspirated psychrometer.

[2]The values have been taken, in the R.H. of 5 to 5 units and in the temperatures of degree by degree.

[3]The average has been calculated by the abbreviated method

according to the formula $y=c\,\bar{u}+y_o$, where y_o is the mark of class origin of work; c, the class interval; u, transformed marks of class from which the value $\bar{u}$ is obtained.

[4] The standard deviation has been obtained starting from the - abbreviated method

$$S= c\sqrt{\frac{I}{N}\sum n_i \; u_i^2-\bar{u}^2}$$

where ni are the frequencies, N the total number of observations.

[5] N.S.Bromelle, Illumination, air- conditioning... in the con - servation of Cultural Goods, "Museos y Monumentos", vol.XI, pp. 309-320. Unesco, 1969.

[6] Control of Museums environment: a basic summary, I.I.C., London, 1967.

[7] It should be pointed out that the fluctuation permitted is ±3 units the R.H., not 3% of the value of the R.H. It may be interpreted mistakenly, thinking that the error is given in so much per cent, whereas in reality it is the R.H. that is expressed in %

[8] The measure of the standard deviation is 3.71 units in absolute value with respect to the central value, which means that the deviation is ± 3.71/2=±1.85.

[9] Cabrera, J.M., and Cifuentes, A.M., "Climatologie au Musée du Prado", ICOM. Comité de Conservación, Venice, 1975.

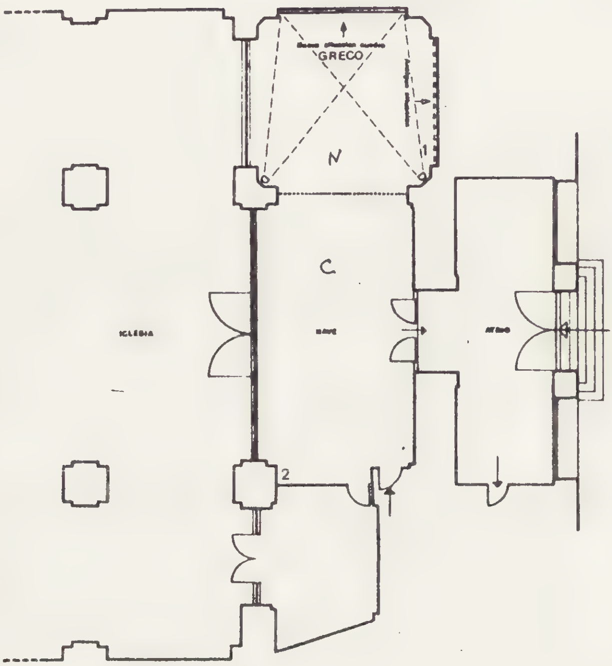
[10] I.I.C.Conference on Museum Climatology. New York, 1967.

[11] Thomson, G., Conservation and lighting in Museums. Information Sheet. The Museums Association. London (2nd edition revised, 1974).

[12] Feller, R.L., Control of deteriorating effects of light upon Museum Objects, in "Museum", vol. 17, number 2 (1964)

[13] Crawford, B.H., and Palmer, D.S., Fuether investigation of colour rendering and the classification of light sources, in "Studies in Conservation", vol. 6, num. 2-3, pp. 71-82 (1961). Thomson, G., A new Look at Colour Rendering, Level of Illumination and Protection from U.V. Radiation in Museum Lighting, in "Studies in Conservation", vol. 6, num. 2-3, pp. 49-70 (1961).

[14] For obvious reasons the equipment installed is not specified, nor are the circuits and terminals detailed.



IGLESIA DE SANTO TOME (TOLEDO)
ATRIO Y NAVE DE EXHIBICION DEL
CUADRO DEL GRECO "EL ENTIERRO
DEL CONDE DE ORGAZ"

Itinerario
Verja
Vidriera
Vidriera opaca
Foco de luz
Haz luminoso

Fig 1

TEMPERATURA

°C	ABRIL C	ABRIL N	MAYO C	MAYO N	JUNIO C	JUNIO N	JULIO C	JULIO N	AGOSTO C	AGOSTO N	SEPTIEMBRE C	SEPTIEMBRE N	AIRE ACONDICIONADO C	AIRE ACONDICIONADO N
8	1													
9	5													
10	6													
11	5													
12	10													
13	17	2		2										
14	25	6		1										
15	26	25		6										
16	72	33	7	4										
17	137	41	35	41										
18	112	118	153	118	33							36		
19	112	125	201	232	62	8						67	122	
20	45	90	99	209	70	37						37	398	194
21	53	71	12	72	55	63						25	153	337
22	6				97	89				1	26	27		111
23					145	169				1	59	61		
24					77	133	1			2	70	62		
25					79	90	10	9		18	109	54		
26					63	61	32	92		49	82	37		
27					15	11	63	151	19	113	59	23		
28							129	146	65	79	84	61		
29							101	169	150	154	50	45		
30							107	105	104	146	50	41		
31							109	5	70	90	46	15		
32							87		102	7	24			
33							74		32	1				
34							111							
35							41							
$\bar{T}$	17'5	18'6	18'8	19'2	22'5	23'3	30'5	28'6	30'1	28'7	26'6	24'2	20'1	21'1
S_t	2'4	1'71	0'97	1'20	2'33	1'73	2'57	1'62	1'58	1'71	2'68	3'83	0'64	0'90

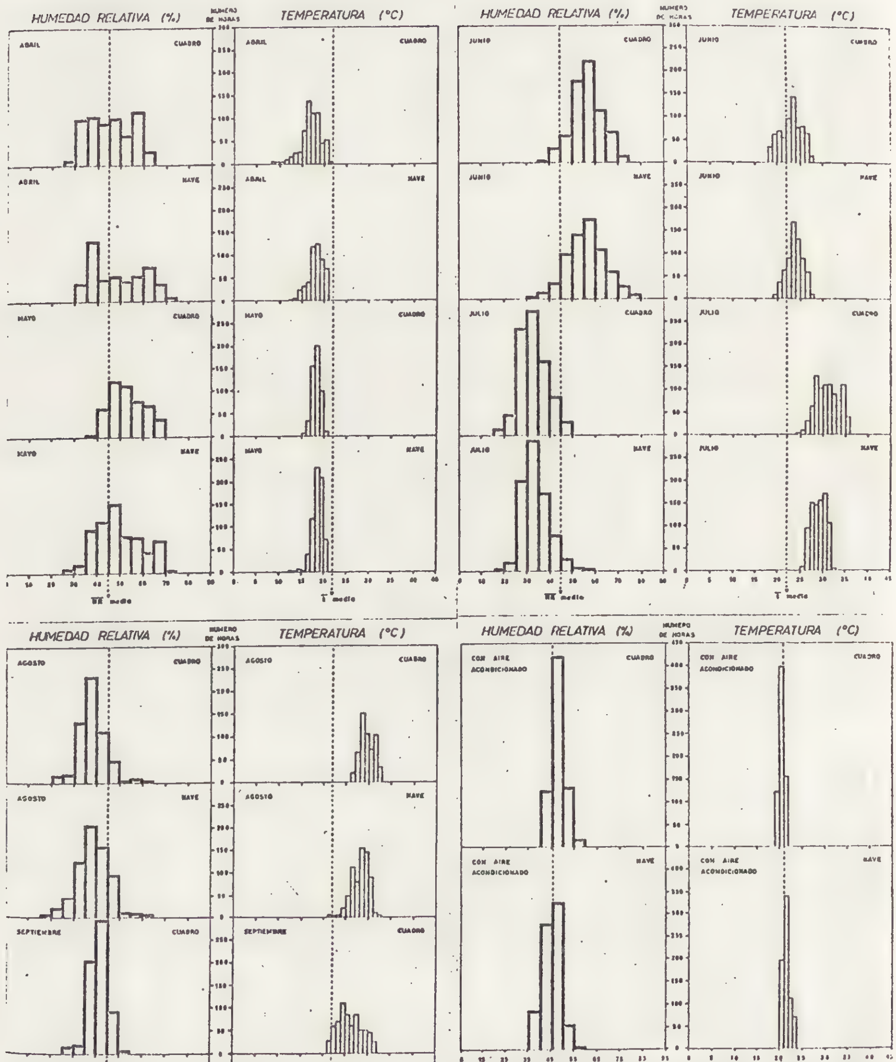
HUMEDAD RELATIVA

% HR	ABRIL C	ABRIL N	MAYO C	MAYO N	JUNIO C	JUNIO N	JULIO C	JULIO N	AGOSTO C	AGOSTO N	SEPTIEMBRE C	SEPTIEMBRE N	AIRE ACONDICIONADO C	AIRE ACONDICIONADO N
17'5							14	4		3				
22'5							46	21	16	19				
27'5	17			11			235	201	17	44	15			
32'5	100	42		18		2	276	288	133	125	20	62		
37'5	105	132	4	94	1	16	162	173	237	206	202	125		85
42'5	90	50	65	113	32	36	84	80	112	157	294	160	124	275
47'5	101	56	124	152	59	99	28	27	49	95	92	174	418	322
52'5	65	46	115	80	177	141		8	2	10	7	57	128	54
57'5	116	57	80	79	221	174		6	7	7		13	16	3
62'5	30	76	69	44	113	111			1	4				
67'5		40	42	69	66	62				3				
72'5		9		4	15	31								
77'5		1				9								
$\overline{HR}$	42'3	49'1	53'3	49'5	56'7	56'4	32'8	33'9	37'8	38'7	41'1	43'2	47'8	44'9
S_{HR}	9'71	11'65	7'56	10'11	6'66	8'36	6'18	6'28	5'92	7'28	4'39	6'11	3'38	4'03

Fig 2

HISTOGRAMAS DE FRECUENCIA

HISTOGRAMAS DE FRECUENCIA



RESUMEN DE DATOS	ANTES DEL AIRE ACONDICIONADO	CON AIRE ACONDICIONADO
HUMEDAD RELATIVA MEDIA	44'6 %	46'4 %
DESVIACION TIPICA MEDIA	7'52	3'71
TEMPERATURA MEDIA	24'1 °C	20'6 °C
DESVIACION TIPICA MEDIA	2'03	0'77

Fig 3,4,5y6

78/18/6

PRINCIPLES OF INTRODUCING OPTIMUM MICROCLIMATE IN ARCHITECTURAL MONUMENTS. RESEARCH METHODS

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PRINCIPLES OF INTRODUCING OPTIMUM MICROCLIMATE IN ARCHITECTURAL MONUMENTS. RESEARCH METHODS

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Architectural monuments, including ancient church and monastic buildings, are not only houses for worship but also objects of museum displaying. The state of monuments and articles of artistic and historic value housed in them depends in many ways on the microclimate inside the buildings. At present, there are no scientifically verified recommendations regulating temperature, humidity, air speed; construction norms and rules for designing heating, ventilating and air conditioning systems, and unified condition research techniques are lacking.

Complexity of meeting this challenge is determined by capacity-planning and architectural-and-constructional peculiarities as well as specific features of building utilization (complex partitioned capacity, bulky guarding enclosure offen having unknown thermal properties, necessity of taking into account the differencies in requirements for comfortable conditions to be enjoyed by people and preservation of artistic objects).

These factors determine the value of specific thermal characteristic and the state of thermal and air conditions of a building and, consequently, the choice of rational heating, ventilating and air conditioning systems.

Dependable information is essential for elaboration of scientifically verified measures to secure the required microclimate within a building - monument. To this end, WCNILKR-KISI of the USSR and NIPK of Bulga-

ria have, at present, improved methods of research covering temperature and humidity conditions in a monument and elaborated techniques to ascertain thermomechanical properties of external guarding protection and to carry out model research in to thermomechanical and aerodynamic conditions.

Complexity of full-scale research and control over parameters of air inside architectural monuments is emphasized by the fact that it is technically difficult and, at times, impossible to measure temperature, relative humidity and air medium mobility in all its capacity size, unlike dwellinghouses, public and industrial buildings where air parameters in the working range area are of major importance. The medium and upper zones of buildings where it is especially difficult to mount and service measuring instruments are most unaccessible for measuring operation.

Investigations we carried out in a number of monuments in the USSR and Bulgaria for many years have proved that measurement of temperature and relative humidity of air taken in the design centre of a building is representative in relation to the entire capacity of a building, i.e. here is no need of taking measurement in other points.

It is recommended, though, depending on climatic conditions (for instance, in Southern or Northern areas), to take preliminary control measurement at Northern and Southern walls so that to justify a necessity of taking measurement in these points. A similar procedure is advisable while furnishing grounds for placing measuring instruments in an altar, chapel and other specific cases.

Measurement of air parameters along the building vertical should be taken in the following sequence.

In the lower zone measuring devices are mounted 1.0-1.5 m. above the floor level and in the upper zone - 0.5-1.0 m from the top. Intermediate points of measurement are determined tentatively. To this end, a temperature sensor is moved from the lower point upward vertically until the temperature reading is changed by 2°C. (Temperature fluctuations of internal air ±1°C envisaged by practical norms are taken into account). Relative air humidity should be registered in the same points as temperature. To take measurement of air parameters in any point along the height of a building a sensor is connected with a pilot-balloon filled with hydrogen or helium. The same principle is applied in this case as the one used in exploration of super-standard layers by hydrometeorological service. Before pilot-ballons go up a researcher is to estimate total weight of control and measuring equipment. Then, depending on ballon volume, the number of balloons (n) is to be estimated:

$$n = \frac{G}{g} \text{ pieces,}$$

where G is total weight of equipment lifted, g;
g is free lift force, g.

The estimated number of balloons should be connected together and a set of sensors to measure parameters of internal air is to be attached. The ballons are lifted by a winch to a preset level and are moved to another point having the readings taken. After measurement the balloons are put down and disconnected from measuring equipment.

The measuring technique and instrumentation have been elaborated by the Chair of Heat and Gas Supply and Ventilation of the Kiev Civil Engineering Institute and tested in laboratory and full-scale conditions.

Internal air temperature and humidity control is recommended to be performed thoughout the year. Annual climatic characteristic is to be taken into consideration (cold, warm, normal, extremely cold or extremely warm).

Parallel with the above, full information about external air parameters should be obtained. Such data can be provided as a result of a researcher's measurement or from log books of neighbouring weather services.

As it was revealed by our tests over these years, observations of internal air parameters may be undertaken periodically, 30-40 days in any characteristic period of the year (winter, spring, summer, autumn).

Instruments used to register temperature are to secure accuracy within the limits of ∓ 1 and air humidity - $\pm 5\%$. Measuring instruments may be different by operating principle and their design. We used electrocompensation balanced bridges, electronic potentiometers with sensors (thermocouples, thermoresistors), hygrographs and weekly-wound thermographs, thermistor thermometers and hygrometers (for example, "Hygrophil" type).

Temperature measurement on the internal surface of a guarding enclosure is of control nature. This measurement is performed in order to define thermal properties of enclosing structures, their effect on air temperature indoors, to check theoretical estimation of heat loss and accumulation. Internal surface temperature is made use of while estimating heat activity coefficient of enclosuring structures which expresses heat conduction - to - heat capacity ratio in a unit of mass being the most important factor of thermal properties of a material.

To measure thermal activity coefficient contact sounding methods may be deployed successfully. The major advantages of such methods are a short duration of a single experiment (about 10-20 minutes) and a possibility to test both dry and damp construction materials.

The suggested technique of measuring this coefficient is based on regularities of unsteady heat exchange between a sample of material to be tested and a probe under the conditions of thermal conjugation of bodies. The advantage of this method is that measuring of thermal properties is arranged directly in a structure without sample selection which is highly important for unique buildings.

Besides, lancet-type measuring sensors and a balanced bridge are used to check analytically obtained correction factors defining what portion of heat liberated by artificial lighting and people at various time periods of these thermal agitation factors is accumulated by enclosure.

Measurement is taken during 8 hours every quarter of an hour, in places where no paintings are kept.

Measurement of air mobility is taken indoors in order to define whether its speed is within the recommended limits of 0.1-0.3 m/sec.

High rate of air speed accelerates aging of works of art. Low air mobility indoors contributes to forming unventilated zones with stuffy air. Control measurement of air mobility is taken by seasons making use of thermoelectroanemometers (for example, "LIOT" or "Wallac"-type) of ±0.05 m/sec accuracy. Indoor air exchange control is performed in accordance with a universally adopted technique.

It was proved by our tests that frequency of natural air exchange for buildings of religious archi-

tecture is 0.4-1.0 per hour.

Distribution of meteorological air parameters in a monument may be assessed making use of a simplified technique. Preset parameters cannot be maintained in buildings having no heating and ventilating systems. Non-uniformity of air parameters in a building is estimated by calculating a difference of peak values measured, defining their values and finding the difference between peak rates and medium ratio of these values.

Non-uniformity of distribution of air parameters is expressed in percentage.

Distribution of air parameters in a building may be regarded as satisfactory if non-uniformity is 10% in temperature, 15% in humidity and 25% in air speed which is in compliance with normative assumptions.

It was demonstrated by a test that the best method to determine optimum air distribution schemes was model measurement. A model should be usually made to a scale of 1÷10 or 1÷20. Since a non-isothermic current of air is studied the pacing similarity criteria are those of Reynolds' (Re) and Archimede's (Ar). In case of constrained air motion going with free air motion conditioned by gravitational forces and speeds of these motions being comparable it is Re, Grasgof (Gr) criterion and Pecle (Pe) reduction criterion that become decisive with interrelation of parameters providing for all model tests to be carried out within the limits of an automobile modelling zone. It is sufficient, therefore, to keep to a geometric similarity in a model. Speeds and temperature of air are recorded.

Visiting public whose number is frequently excessive for a given capacity is one of the most serious factors changing stability of microclimate in a monu-

ment. When there is no OVK system to make the visitors' effect less a strict regulation of both their number and period of staying inside is essential.

Estimation of the visitors' number is made in accordance with the formula below:

$$h = \frac{v\,(d \;\cdot\; d\,)\cdot k \cdot j \cdot 60}{Z \cdot g} \quad \text{men} \quad (1),$$

where v is a building's capacity, m^3;

d , d - initial and final moisture contents of air correspondingly, kg/kg;

k - frequency of air exchange equaled to one per hour;

j - air volume mass, kg/m^3;

60 - minutes;

Z - time of visitors' staying in a hall, min.;

g - moisture quantity dozed by one visitor per hour, kg/kg.

Microclimate investigations have been carried out in a number of architectural monuments in the USSR and Bulgaria making use of the above methods. Their results were deployed in designing microclimatic systems for the Boyan church (13th century), the churches of St George (4th century) and St Petka (15th century), the Cathedral of the Birth of Our Lady in the Chernigov District and the Cathedral of the Prophet Elijah (17th century) in Yaroslavl.

78/18/7

INVESTIGATION OF MUSEUM EXHIBITS BY ELECTRON PARAMAGNETIC RESONANCE

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5th Triennial Meeting
Zagreb, 1978

INVESTIGATION OF MUSEUM EXHIBITS BY ELECTRON PARAMAGNETIC RESONANCE

S.S. Ishchenko and I.G. Yavtushenko

Investigation of museum exhibits is carried out now and the most various branches of science and engineering joint it. There are different physical, chemical and physicochemical methods that enable to get various characteristics of matters in the arsenal of the investigators. So microchemical, emissive, spectral, x-ray structural, neutron-activating and other kind of methods are used to determine composition of exhibits. Quantitative and qualitative change in the structure of molecules in matter on atom group level is observed by infrared spectroscopy. Ion--exchange chromatography enables to carry out identifications of albuminous binders. These and others methods of investigation enable to study exhibits more successfully.

However, having such a variety of analytic methods of studying museum exhibits in existence, the methods mainly submit to solution of the tasks that are connected with attribution and restoration of exhibits. Besides the newest achievement of science and engineering are used not enough to determine and create optimal conditions and methods of exhibit keeping that considerably increases efficiency of the prophylactic measures.

The absence of quite subtle methods of studying the destruction mechanism itself has serious consequences.The usage of spectral methods (ultraviolet,

x-rays and so on) mentioned above has the particularity that the methods of the investigation operate by comparatively high energies against the backgroud of which the interactions characterizing the state of electron coupling and microstructure of a matter are lost. The information on the interactions can be obtained through microwave spectroscopy methods the resolution of which enables to fix comparatively small sorts of energy.

We suggest to use for investigating museum exhib bits one of the microwave spectroscopy methods namely the method of electron paramagnetic resonance (EPR). The EPR method was found out by the Soviet scientist Ye.K.Zavoisky in 1944 and now is used more and more widely.

A corresponding experiment was made to determine the efficiency of the investigation the method suggested. Experiment was made with a EPR spectrometer operating in the 3 sm wavelength range in the Microwave Spectroscopy Department at the Ukrainian SSR's Academy of Science Institute of Semiconductors. Spectra of absorbing microwave power from the objects on the different materials such as wood, canvas, paint, paper, ceramics, smalt and others were registered. These spectra carry an information on the matter's microstructure and permit to fix its changes on the electron level.

Analysis of EPR spectra show they are due to paramagnetic ions of manganese, iron and other elements that are the components of the main matter or are in the matter as impurities and also by radicals -

electron of broken chemical bonds. The latter are of immense interest as one expects that production of the radicals is in the direct connection with the mechanism of ageing and deterioration of structural organization of substance.

Fig.1 presents the EPR spectra from different elements of a picture: a - canvas, b - canvas and priming, c - paint. It should be taken into account that the spectrum of broken electron bonds (radicals) has been found in the canvas. Doubly charge ions of manganese are perfectly observed in the EPR spectrum of priming.

The dependence of EPR spectra on different factors (light, temperature, radiation and so on) has been investigated.

Fig.2 illustrates the EPR spectrum of canvas before (a) and after (b) 30 minutes' intensive illumination by the xenon lamp. The rate of increasing radicals in the canvas can be seen by the spectrum's lines depending on the light action.

Wood also shows the analogical dependence of increasing radicals on light action (Fig.3).

More intensive appearing of radicals became apparent while acting on an object by γ radiation. Fig.4 gives the EPR spectrogram of new wood before (a) and after (b) γ radiation (dose 15 Mrad).

Fig.5 has its purpose to illustrate the connection of ageing of substance with the presence of radicals in it. Looking at the fig.5 one can see EPR spectra from: a - new canvas, b - new canvas after γ

radiation (dose 15 Mpag), c - old canvas.

The results that have been obtained suggest the use of EPR method to control the microstructural changes of the relict's matter on the electron level. According to the presence of the radicals in the spectrum one can determine speed and rate of destruction this or that material depending on the different factors. This, in turn, will help to define more exactly optimal regimes of keeping exhibit group of similar material or some especially unique museum monuments.

The method suggested is most likely to give the possibility defining more exactly the tolerant dose of acting with different methods to study exhibits particularly connected with ultraviolet, roentgen and other kinds of radiation.

Now the work on use of γ radiation in struggle against biological vermins of exhibits, of paper in particular has been begun. Taking into account great paper subjection to structural changes through acting γ radiation we'd like to warn against the method that demands additional careful control.

EPR spectra obtained from investigated objects carry marked imprint of individual properties inherent to electron structure only of the present object. This is likely to permit successful use of the EPR method resolving complicated questions of identification. The spectra of red smalt are given in the fig.6. Two of them (a,b) tell that the samples are of the same composition but one of them (c) has distinctive

structure.

The potential capabilities of investigating museum exhibits by EPR method can be put into practice when some laboratories take part in this work. EPR spectrometers are produced serially by some countries. They are "RE 13-06" - USSR, spectrometers of firms "Varian" - USA, "Jeol" - Japan, "Bruker" - FRG and other.

Ready to get into scientific contacts in the investigation using EPR method, we are waiting for suggestions.

CONSERVATION OF LEATHERCRAFT AND RELATED OBJECTS

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Programme 1975-1978

1. To promote responsible conservation and restoration of leathercraft products and artistic and archaeological objects of leather as well as other related objects through communication among the members.
2. To encourage the exchange of experimental findings or other relevant information providing this does not interfere with the sovereignity of a particular work or with the priority reserved for the publishing of this findings.
3. To examine the merits of available methods and to develop new ones in matters concerning the salvage of dry, pulverising archaeological leather finds (Szalay).
4. To broaden the knowledge on leather manufacture in order to obtain a better understanding of the causes of leather decay, especially the red rot (Reed, Chahine, Van Soest).
5. To study the conditioning of leatherwork with respect to exposition and storage (Gibson, Reed, Guilly, Løken).
6. To refine the composition of leather dressings employed in the treatment of decaying leather (Schaffer, Schmitzer, Clarkson, Tilbrooke).
7. To assess existing training programmes and to stimulate their development by propagating them as well as by translating the instructions on which they are based into various languages (Gibson, Schmitzer).

WORKING GROUP CONSERVATION OF LEATHERCRAFT AND RELATED OBJECTS

Coordinator: T. Stambolov

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INTRODUCTORY REMARKS

A close survey of the leading American, Russian, French and German journals on leather manufacture and maintenance has shown that since the last ICOM-Conference in 1975, in Venice, there have been no publications which could further the interests of proper conservation of leather objects of art or leather artifacts.
Monographs dealing with this subject are, to the best of my knowledge, also lacking. However, a Nordic Extra-Mural Course on the conservation and restoration of leather, skin and parchment, held at Kulteren in Lund (Sweden) from April, 4 till April, 14, 1978, organised by the Working Committee (Mr. Fred Allik: Kulturen, Lund, Sweden; Miss Marianne Carlsson and Mrs. Margaret Myers: Det Kongelige Danske Kunstakademi, København, Denmark) compensated this deficiency by the revealment of facts and relevant instructions and suggestions referring to artistic, archaeological and bookbinding leather. The proceedings of this course are soon to be published and copies could be obtained from the aforsaid Working Committee.
The reports discussing the care of various types of leather and related matter as for instance fur, that are to be presented at this session of the working group , have undoubtedly in common the quite new approach to the problems of conservation they intend to cope with. That is to say, the authors have worked in accordance with the necessity first to detect the facts of deterioration to study their causes and understand the scientific explanations that could be given for them and only then to proceed devising modes of treatment and formulating media with which to attain a responsible and well-founded salvage of the objects in question.

The reports must, therefore, be regarded as an illustration of the working groups's programme that since 1975 is the guideline of activities in this field.

In this report an adequate illustration of the programme's proclaimed intention to promote responsible conservation and restoration of leather objects in particular, is the 45 minutes lasting film "Dutch Gilt Leather" by Mr. P. de Haan, a cinematographer at the Central Research Laboratory for Objects of Art and Science, Amsterdam, Netherlands.

CONSERVATION OF LEATHER OBJECTS IN HUNGARY

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CONSERVATION OF LEATHER OBJECTS IN HUNGARY

Zoltán Szalay

Recently considerable results have been achieved in the development of conservation and restoration techniques of leather objects in Hungary. We have tried to dispense with empiric methods. We have studied the properties of prepared leathers and the various kinds of damages they suffered. To a certain extent we are already able to make inferences concerning the grade of deterioration. We apply two methods of examination.

/1/ We mount a thin cutting of the leather object to be treated and examine the refraction of collagene fibres with a polarization microscope.

/2/ The examination of materials extracted by water from unearthed leathers with paper chromatography. This is a test first of all for tanning agents and soluble proteins, amino-acids. It is the quantity of proteins in the resulting solution from which we can mainly conclude on the extent of deterioration.

To arrive at more exact results we need more data. They should include the results of the tests, the method of conservation and its result. As we do not yet have at our disposal sufficient testing possibilities and figures respectively we have also to take into consideration some factors of uncertainty. It may, of course, affect the success of conservation. It occurs sometimes that the leather reacts in an unusual way to preservatives.

The role of water in maintaining the elasticity of leathers

The basic material of leather is collagene, to which water is linked chemically. This comparatively instable bond easily dissolves, in response to outside action. Leather objects also contain water taken through capillary attraction. The quantity of such water greatly depends on the effect its surroundung has on the object. Water keeps the collagene fibres far from each other and somewhat also swells them. The extent of swelling is also subject to the degree of tanning of the collagene. In perfectly dried leathers the bonds between collagene and water are disrupted and cannot be restored.

If the chemical bonds between collagene and tanning material break, the collagene fibres can take more and more water as a function of the broken bonds. The water thus taken continues hydrolysing the bonds between collagene and tanning agent in the wake of which the peptide bonds of the collagene becomes vulnerable. As such

a collagene fibre can take much water, the hydrolysis of peptide bonds also starts, which is actually a slow glutinization. The proteins so decomposed dry crustily against the collagene fibres and are therefore to be dissolved and removed from the leather.

Having sized up the foregoing, we are to face the following problems:

/1/ The moisture contents of the leather must by all means be stabilized as the injured collagene fibres are no longer able to perform this task. We hafe to find a stabilizer fit for bringing about an equilibrium with both the external and the internal environment.

/2/ If we meet the above requirement, there will be two damp-absorbing systems in the leather: the collagene itself and the stabilizer. Under such circumstances it is unimaginable that, with the changing humidity of the environment, a stable equilibrium comes about in respect of the leather. Now we can do two things. We can either stabilize the humidity of the environment, or protect the damp-abrosbing system of the leather from outside effects. The best is, of course, if we can do both. As, however, the former one fully depends on the local circumstances, we must, by all means, accomplish the protection of the system for stabilizing the water contents.

/3/ It is beyond doubt that the decomposed protein particles must be removed from the leather. This procedure has the advantage that at the same time other harmful materials, too, can be removed. In case of leathers treated with alum it has the disadvantage that the greater part of the alum steep, too, leaves the leather. Such leathers are to be tanned again. In leathers of bark tanning the surviving fibres remain intact but, depending on the quantity of eluted materials, these leathers will become more and more "empty". It is comparatively easy to soften such leathers but their mechanical stability will greatly decrease. As a result of internal friction the fibres may break. The leathers will look flabby and will stretch irregularly. Accordingly, they are to be "filled" with some aggregate so that they will not lose their leathery character.

/4/ In leathers where the glutinization process is in an advanced stage the fibres yet saveable are to be stabilized first of all, that is, they must be made insoluble in water.

The conservation of painted, gilded and embossed leathers and leathers combined with other materials like textile, parchment, metal or wood, undoubtedly presents several other problems but in the course of our work we accepted the aboves as basic principles.

When restoring a leather object we aim at gluing and completing without mutilation. The texture and appearance

of the completion must fit harmoniously to the original parts of the object. It is very important that the completion move exactly like the original material when folded otherwise ugly breaks may come about at the seams.

We tried to stabilize the water contents of leathers with several materials but funally have reverted to glycerine. The remarkable fitness of glycerine for stabilizing water contents may perhaps be deduced from its false tanning effect. The main problem is the regulation of the quantity of glycerine. If the quantity is insufficient, the leather remains brittle. Too much glycerine, on the other hand, will make the surface of the leather dark and slimy. Finally we simplified our procedure to applying an overdose of glycerine then removing the surplus by solution in tertiary butyl-alcohol.

This double system for stabilizing the water contents is, for the reasons set forth above, very sensitive to the fluctuations of relative humidity in the environment. Therefore it must be protected. Various fats, oils, waxes, and wax-like alcohols are suitable for this purpose. According to our experiences the greasing of leathers with emulsions gives the best results. For emulsor we usually use sulfonated hoof oil but in certain cases we employed with success methyl-cellulose, on other occasions carboxy-methyl-cellulose. On account of the several differences, the various shapes of leather objects, we treat each as an individual piece. We can describe some basic procedures never excluding the possibility of necessary modifications from case to case. We strongly stress the importance of proper drying. In fact most procedures for conserving leathers will be a success or a failure subject to the method of drying. In the course of our experiments we followed the move of materials in the leather with exact measurings. It was observed that if a leather object is dried after treatment so that it is in contact with the air on all sides to the same extent, then the materials taken in will move rowards the edges. This move is all the more intensive the weaker, the "emptier" the leather is. Therefore we decided to always dry leather objects between blotters.

The procedures of conservation given here can be applied with satisfactory result in very many cases.

Leather objects in the course of excavations must be protected against running dry. The object is packed in wet paper wadding, on which we drop a few drops of Oleum Thymii to avoid mould formation. Then it is packed in polythene foil. We should never forget to fasten the identification tag outside of the package. Leather finds are to be treated promptly. First of all we soak the leather object in a 2-3% solution of fatty alcohol sulphate for 3 to 4 days. The soak is changed every day. If the soak gets very thick and brown in a day or does not

stay cleanafter a few days of soaking, then the leather is water soluble. The situation is ever worse if the object suddenly swells during soaking. This means that the glutinization of the leather is in an advanced stage. Such leathers are taken out of the soak immediately and are dried between blotters until they are still pliable. Then they are treated wiht butyric acid /2% of the leather's weight/ to which we add 1% ammonium lactate. The butyric acid will precipitate the collagene ceasing thereby the solubility of the leather in water. Depending on the thickness of the leather this operation may take anything from a few hours to 48. The quantity of the acid must not be increased as too much acid will reverse the process. The superfluous remainders of butyric acid are to be neutralited with tertiary butyl alcohol. This ensues when the unpleasant smell of butyric acid has ceased. Then the treatment is to be finished with one of the following procedures.

Procedure No. 1.

We dry the leather between smooth filter papers until it loses its shine received from the reating material. We daub its both sides with a 50% glycerine solution sparingly and wait until the glycerine gets absorbed. Then the leather is treated on with the following emulsion:

50 gs of lanoline,
150 gs sulfonated hoof oil. We strongly stir the liquid and add

100 gs of hoof oil,

and finally mix it with

3 gs of Oleum Thymii.

We cool the solution and impregnate the leather with it. After this follows final drying between smooth filtering papers.

Procedure No. 2.

If the leather find is of a shining surface, it needs further treatment. In such a case after the above treatment we

melt one part of beeswax, to which we add
two parts of paraffin wax.

When this, too, has melted, we take it off the stove and add so much white spirit that the pour test will be lubricable. When soaking shows that the glutizination process has not yet started we employ another procedure.

Procedure No. 3.

With this procedure we can reach almost any grade of softness. The clean but still wet leather is to be smeared with 50% glycerine on both sides. When it has been

absorbed, the leather is put in the following mixture:

One litre of warm water,
170 gs of hoof oil
200 gs Turkey red oil
15 gs lanolile
50 gs 1550 polyethylene glycol.

Before using we cool the mixture down to room temperature. We keep the leather in it for from 10 minutes to half an hour. Then we put it into the mixture of

250 ml tertiary butyl alcohol and
20 gs cetyl alcohol or myristil alcohol

In most cases the leather will get too soft in the first soak. In the alcoholic mixture the process is just the reverse as some of the materials taken in from the former solution will be eluted by the tertiary butyl alcohol. This is why we are to go on folding and bending the leather until we feel that it has reached the desirable pliability. The disadvantage of this procedure is that after this the leather cannot be stuck. If sticking is unavoidable we have to apply the following procedure.

Procedure No. 4.

First the object is to be put in a 50-50% mixture of glycerine and water for at least half an hour so that it will be soft, then it is soaked in the following mixture:

1500 ml t-butyl alcohol
36 gs myristil alcohol
20 gs hoof oil
2 gs pentachloro-phenol

The superfluous glycerine then will be eluted from the leather. Otherwise we do the same as in the former procedure. If we omit the treatment with glycerine, this method is suitable for the treating of such leather objects from the Middle Ages or later periods which have not yet lost their fixed water contents.

Procedure No. 5.

This has been elaborated for the treatment of alum-tanned leathers recovered from crypts. By the weight of the leather to be conserved we take

10% alum
7% sommon salt and
2% semolina.

We put the leather in their aqueous solution. We add water until the solution covers the leather. It is kept here for 8 days then dried. Drying takes a week. Then we wet the leather, thoroughly knead it, smear on it a thin layer of 50% glycerine then fat-liquor oil. The ingredients of the fat-liquor are:

10 gs hoof oil
20 gs sulfonated hoof oil
1 g lanoline
0.5 g cedar oil

all mixed in one litre water.

Then the leather is dried on shape between blotters.

Sticking

After conservation sticking and completing may follow. In every case we strive for a solution that does not include the mutilation of the object. With this aim in view we elaborated a process of sticking the torn parts into edges. For this purpose we use the silicone based adhesive "Elastosill 07" manufactured by the Wacker company. The adhesive dries in contact with air, it is elastic and cannot be absorbed in the leather. In case of more heavy objects the sticking must be reinforced. We cut with a sharp knife the edges stuck slantwise and crosswise on the flesh side of the leather. We put strong linen flax yarn into the cut then stick back the cut leather with Elastosill 07.

Completion

We make a silicone negative of the surface of the conserved leather. We find a surface which is similar to the part to be completed. Then we prepare the stuff for completion. We put eart colour of a suitable colour into polyvinyl acetate dispersion plus not more than 5% well shredded asbestos wool and stir thoroughly. Then we properly adjust the silicone negative and put the part to be completed with its grain side on the negative and stick its edges on the negative with lanoline. Now we can still stick in their places the fragments if any. Then we smear with a wide plastic shovel in the place of the missing part, the prepared stuff for completion. When this mass is put on in a thin layer we press it with a soft polyurethane sponge and let it dry. It can be removed from the negative after perfect drying only. The superfluous lanoline can be removed by dissolving with white spirit. In case of bigger completions we can include linen flax yarns in the edges of the completions. The surface of the completion can be treated with the same materials as the original leather surface.

The few procedures treated in my report constitute only a small part of our activities. The aim of these few words was nothing more than to give an outline of our research work and our principles of restauration.

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GILDED LEATHER

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GILDED LEATHER

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Concise history of the gilded leather industry. Spreading of the use of gilded leather as a wall-hanging from North Africa via Spain to the Northern and Southern Netherlands.
Restoration and conservation of gilded leather, a chapter in which the restoration methodology, the restoration materials and the working methods, as applied by us, are discussed.
Impregnation of gilded leather by means of epoxy resin.
Applied scientifical research in connection with gilded leather.

INTRODUCTION.

It is not easy to derive from its name that, beside leather, the main component of gilded leather is leaf-silver. But, by spreading two layers of yellow varnish over the silver-layer the gilded leather maker attained a golden splendour of an intensity that could not be achieved by the use of gold-leaf. In as early as the 14th century gilded leather was in Europe made in this way, although differences in working-techniques did of course arise.

The making of gilded leather is probably of Arabic origin. There is a book on geography, written by Ebn'Abd el-Noûr el Hamiri from Tunisia in the 6th century of the hegira (1122-1222), in which Ghadâmès is named as the town where 'el-djild el-Ghadâmesi' came from. The word Guadamacil, later used to denote gilded leather, is derived from (the town of) Ghadâmès. It may be assumed that already this leather of Ghadâmès was gilded leather.
It was the Moors who introduced and afterwards controlled the making of gilded leather in Spain. The gilded leather industry there was centred, from the 14th century on, in Cordova, but other towns too, such as Sevilla and Barcelona, were known for their gilded leather industry. In Barcelona the gilded leather makers were already in 1316 united in a craft-guild. Gilded leather was in Spain made till about 1630. After 1630 the best days of the gilded leather craft were over, and it may undoubtedly be seen as a result of the evicting of the Moors by Philip III in 1610. After their eviction from Spain many

Moors settled down in Venice, which was the centre of the gilded leather industry in Italy in the 16th century. Then Flanders took over the position of Spain and was thereafter famous for its gilded leather all through the 17th century, the town of Mechlin being the main center that had contributed a great deal to this craft.
Gilded leather was exported to all parts of the world from the middle of the 14th century.
It is Guicciardini who, in his description of the Netherlands, mentions that in 1567 the processing of leather was by far the most important trade of Mechlin and that a quarter of the townspeople lived by it and that it occupied a seperate part of the town, with buildings, water-routes and canals of its own. Set up in such a way, the making of gilded leather became soon one of the town's main resources. The first gilded leather maker in Mechlin is reported in 1511. Gilded leather was in Mechlin made till about 1800. In the Northern-Netherlands it was The Hague, Amsterdam, Dordrecht and Middelburg that were known for their gilded leather makers.
The gilded leather maker Jacob Dierxsz de Swart from The Hague was the one who contributed much to the replacement of a by then already obsolete decorative method, namely, the ornamenting of leather by means of hand-dies. He introduced the method by which the leather was printed in relief by means of wooden forms, carved in the desired pattern. This method gave the Dutch gilded leather an exceptional fame, but, nevertheless, the Dutch gilded leather came to an end after 1680, as by then people appeared to chose more and more for painted wall-paper on linen as a wall cover. The subsequent competition made the gilded leather makers look for new production methods. There came strips of panels of gilded leather bearing over the whole of the surface one and the same print, the panels being adhered together and of a length of up to 4 meter. In this way it was possible to work faster. Gilded leather wall-hangings of panels, glued together, with a size of 5 x 6 meter are still preserved to the present day.
The usual design made way for new ones. There exist, e.g., paintings on linen that resemble so much the paintings on leather that it is only after very close observation that one can perceive the difference in material.
This method was however disastrous to the gilded leather makers.
In the end a gilded leather product was made that could just as well be produced on linen, but was quite difficult to sell, since the one executed in linen was much cheaper. This kind of gilded leather was made till circa 1781. It appears from accounts that this type of gilded leather was supplied via intermediary agents, and this might be an indication that the making of gilded leather was finally restricted to the Southern-Netherlands or to France, where, according to records, gilded leather makers were active.
No more gilded leather was sold after 1800, and if there are invoices, referring to this business, they almost always have to do with the removing of gilded leather from rooms.

WORKING METHOD.

Apart from the difference in ornamentation and decoration, the making of gilded leather remained the same for centuries. One can find, however, differences in working-techniques that are characteristic for the period in which the gilded leather was made.
The earliest method, as already mentioned before had as main principle the processing of the front side of the leather by means of small hand-dies. The Dutch invention abolished this age-old technique and subsequently the leather was printed in relief by means of negative wood-carved masters.
Both techniques used the so-called "samsons" (size 75 x 65 cm). These samsons were leather sheets of which only the middle, that is, the best part, was used. The sheets were sewn together as wall-hangings for the space that had to be decorated in this manner and nailed to the lathing on the wall.
After 1700 the samsons were, as already stated, glued together, but, the processing of gilded leather went in essence unchanged and as follows:
After the tannage, the thus produced leather, irrespective of its sheepskin-, goatskin- (Italy, Spain) of calfskin-origin, was furnished with a coating of silver-leaf. Then the silver was polished with an agate and covered with egg albumen in order to prevent the forming of silver-sulfide, and subsequently, two layers of yellow varnish were spread over the silver-layer.
Sometimes the silver was left unvarnished. By spreading the yellow varnish over the silver the gilded leather maker attained a golden splendour of an intensity that could not be achieved when using gold-leaf. On this carrier, finally, the desired decoration was done in transparent or covering paint. However, prior to the decoration, the leather was either treated with hand-dies or printed in relief or printed over the whole of the surface by means of a mangle. In every case the leather had to be moistened somewhat, in order to yield to the print or relief and keep it so after drying.

RESTORATION AND CONSERVATION.

Working method.
Irrespective of the type of gilded leather, we (e.i. The Central Laboratory) always base our restoration-method on the principle that the restoration must be reversible. In other words, it must always be possible to remove additives, without damaging the original. It is also our opinion that, if there are lacking parts to be filled up, a clear distinction should remain perceptible between old leather and new, whereas at the same time the gilded leather as a whole should impress the spectator as being a unity.
For the filling up of such lacking parts and the repairing of tears and holes vegetably tanned calfskin is used.

RESEARCH.

In order to find out more about the materials and techniques applied in the making of gilded leather in different periods, and to get an impression of the condition of a certain leather restoration object, chemical analyses are carried out by our analytical department, in close co-operation with the leather restoration department. For this purpose standard research techniques are used.

By means of X-ray fluorescence spectometry one can at once establish whether the leather in question is chrome-tanned, or, otherwise, e.g. vegetably tanned. It is possible, without any preliminary treatment of the sample, to determine the chrome content in the leather sample. The components of the metallic foil, which lays between the leather and the layer of varnish and pigment-coating, are examined by the same technique. The metallic foil was as a rule on the original gilded leather of silver-leaf, but, on 19th century imitation gilded leather an effect that resembled silver-leaf was often attempted with cheaper materials, such as tin-foil or a compound of lead and zinc. Another X-ray technique, namely the diffraction (with which the crystal structure of a material can be determined), is used to examine the pigments in the applied paint, the salts in the leather and any possibly present corrosion products on the metallic foil.
Determination of the acidity (i.e. the pH-value) of the leather is also carried out. The pH should, as far as leather is concerned, lie in between 3.0 and 6.0. Above 6.0 the leather is too basic and vulnerable to bacteriological and fungoid growth. With the help of a weak acid the pH is reduced, of necessary. With a pH of under 3.0 the acidity of the leather will be too high and decomposition of the fibre will be the result. In that case the pH is increased by means of a weak base, e.g. ammonia. We have learned in practice that too low pH-values occur rather often. It was concluded that the cause for this was to be found in the accumulation of sulfuric acid in the leather (H_2SO_4). This sulfuric acid is formed from the sulfur dioxide gas, which as an air pollutant is readily absorbed by the porous leather. Other causes for the presence of sulfuric acid are also possible, such as presence in the leather of certain tan substances, which, under favourable conditions are transformed into sulfuric acid, according to the equations:

$$2SO_2 + 2H_2O = 2H_2SO_3$$

$$2H_2SO_3 + O_2 = 2H_2SO_4$$

Sulfuric acid thus formed is a strong oxidising agent. It disintegrates the protein chains of which the leather fibre are made and leads to the conversing of the amino acids to ammonium salts, particularly ammonium sulfate, a white powder, which is deposited in the leather.
Determination of the sulfate content in the gilded leather.
By measuring the quantity of sulfate, it is possible to gain insight in to what extent decomposition of the leather fibre already might have taken place. In some samples of gilded leather ammonium sulfate was found in a concentration of up to 20%, which indeed indicates a considerable structural distortion.
Determination of the fat content in the leather.
The fat content in the leather should be kept between strict limits to ensure a proper flexibility of the leather. Chemical as well as physical processes, during the finishing process, can be the cause of a too low fat content in the leather, or, in some cases, that fat content can also be too high as a result of excessive treatment of the leather with fats or oils. Determination of the fat content is, therefore, indispensable for the restoration planning and is done by means of the usual analytical procedures.

Determination of the percentage of moisture in the leather.
As the water content is necessary to keep the leather fibre swollen to an extent that guarantees a proper texture, the capacity of the leather to absorb and to evaporate moisture under fluctuating atmospheric conditions must be studied and investigated.

CONSERVATION.

When the acidity (pH) is found to be too low we can correct this by the use of vapour of ammonia, which is a very simple treatment.
In a closed space, ammonia of about 35% is poured in a basin. The strips of leather that need this treatment are hung in this space by means of clips for about 20 minutes. In this way the pH, if 1, 2 or lower, can be corrected to 3, 4 or 5, as according to the type of leather and its condition. In this way the leather fibre is being prevented from decay by the sulfuric acid that could be produced through the combination of sulfur trioxide with water. Afterwards one can grease the leather, using fat emulsions.
It occurs in many cases that the leather contains a fat content of 1% or less, whereas actually 3 to 4% is necessary. This might cause a severe grain rupture in the leather fibre. We compose therefore, in order to condition the leather properly, our fat emulsions in such a way that after application the leather finally contains about 3 to 4% fat.
The fat emulsion commonly used by us contains distilled water, 20% lanolin, 50% neatsfoot oil, 20% castor oil and 10% Turkey red oil. These ingredients are emulsified in the water by Lerolaat N 100 (=Bayer), an emulsifying agent. The aim that we pursue is to compose an emulsion with 10% fat. It must be ensured that the leather is clean of dust, before dressing with the emulsion. This is done with the help of a short-haired brush, and after that the emulsion is applied to the back side of the gilded leather. If the leather is too dry, a 65% solution of Sorbitol ($C_6H_{14}O_6 \cdot \frac{1}{2}aq$) can additionally be applied in order to increase the uptake of waterdamp by the leather and to keep it in there. Sorbitol serves as a humectant and is used to control the moisture content of the leather, irrespective of possible fluctuations in the humidity. This treatment also limits the shrinking-process in the leather.
If the fat content is of such a percentage that no correction is needed, only distilled water is used to clean the reverse side of the leather, or distilled to which, depending on the moisture content of the leather, Sorbitol is added. Also fungicides might be added if, as a result of an earlier restoration, the gilded leather in question has been infested with fungi growth. This could be expected in cases where, in old restorations, the relinings were glued with rye-flour, which is a feeding medium for mouldy growth. Nowadays both the relinings and the rye-flour-glue are removed, whenever they are encountered during restoration, but there is always a chance that some residues remain in the fibre of the leather. However, in most cases it is not difficult to remove those rests from the leather. The removal of the rye-flour-glue is done with a sponge. dipped in a liquid mixture of a 65% solution of Sorbitol and a fungicide. Then, in order to prevent the leather from warping, it is dried under pressure by means of sand-bags.

RESTORATION.

When restoring gilded leather one is frequently confronted with the consequences of what might be called "leather fatigue". Old leather, e.g., is much more sensitive to changes in humidity than new and will therefore also stretch and shrink to a greater extent. The gilded leather wall-hanging is usually nailed to the wall, and sometimes torn near the nailes as a result of the shrinking and stretching. When nailed too tightly, the leather may also often be torn in other places than around the nails. In order to prevent that this should happen again after restoration, the gilded leather is sewn to an elastic material (such as lycra tulle, which is a segmented polyurethan fibre) and this material, instead of the leather itself, is nailed to the wall.
Accordingly the leather can now "work" without tearing itself to pieces. In order to study the elastic properties of the lycra material a yield-power diagraph was obtained by testing it with a Zwick (Zwick & Co. K.G.) electronic dynamometer.
Gaps, crevices, etc. in the gilded leather wall-hangings , whenever found, are filled up with new leather. We use for that purpose a vegetably tanned type of calfskin, which we dye or paint with materials that are specially designed by BASF for use on leather. We think, however, that in an accomplished restoration a clear distinction between old leather and the complements new leather should be secured, whereas at the same time the wall-hanging as a whole should, nevertheless, impress the spectator as being a unity.
The calfskin, to be used for the relining of tears and holes, must be skived, which means that the edges of the leather patch are made thinner in order to prevent perceptibility of the outline of that patch on the front side of the leather. Here too, the glue used is a polyvinyl acetate adhesive. The front side of the gilded leather, that is the side provided with varnish and the paint layers, is cleaned with an emulsion containing trichlorotrifluoroethane, demineralized water, Lerolat 100 (a nonionogene surface-active agent) and carboxylmethyl-cellulose (C.M.C.); the latter keeps emulsified dirt in the solution and prevents it from precipitating on the painted surface again. The emulsion is carefully rubbed with a soft cloth over the surface of the gilded leather and then the dirt is taken away with another, clean, soft cloth. When performing this work one should wear a mask provided with cartridges that are suitable to prevent inhalating of the harmful trichlorotrifluoroethane vapours. If the varnish and the paint are affected stronly by moisture, which usually appears as a white efflorescence on the surface, a mixture of hexane with a small amount of lanolin, cedar wood oil and wax is used as a cleaner. Hexane regenerates the varnish and takes the white efflorescence awaym whereas the wax and lanolin are used to fil up the subtle crazes so that varnish and paint regain their mild lustre. After the gilded leather has been treated in this way, the separate panels can be sewn together again. It is important, for the sake of authenticity, to preserve the sewing-seams. If consolidation of the panel frieze is necessary, relining of them might be the best solution. Another possibility is the sewing of bands of textile to the inside of the hems.

IMPREGNATION OF GILDED LEATHER.

Impregnation is, in general, the ultimate method to prevent desintegrating leather from getting lost. As with this method an aliphatic epoxy resin with a cyclo-aliphatic hardening-agent is involved, it is a non-reversible one. We have applied this method on a 19th-century gilded leather wall-hanging with an acidity of pH 3.4 and a very high percentage of ammonium sulfate as a consequence of the sulfuric acid present in the leather. This had ruined the fibre structure totally. Also the connection between the grain side and the flesh side was gone, with the result that the painting had become separate from the underground. As it was impossible to save the gilded leather with the restoration methods we know, we chose for impregnation. The restoration completed, it appeared to have been a good choise. The impregnating-agent we used was recommended to us by one of our collegues, who had previously used it with good results for the impregnation of wood. It is a two-component product and mr. Munnikendam gives a further explanation of its chemical composition and characteristics in an article published in "Studies in Conservation" (see notes). Practical advantages of this product are the very low viscosity and a very deep and thorough impregnation. The mixing of the two components causes hardening of the resin and thus brings about a thorough enclosure of every fibre that has been wetted by the resin. This is a considerable advantage as the products that we know so far dry or harden in a manner that allows them, when still in liquid form, to come to the surface, which eventually results in consolidation of the surface only.

The applience of this resin on gilded leather is very simple. The back side, which is the flesh side, is made dirt-free. Paper, glue-residues and other contaminations are removed, so that the impregnating-agent can easily penetrate the leather. Subsequently, the leather, with its painted side down, is laid on a foil of melinex (a polyester resin). The only thing then is to spread, but sparingly, a proper amount of the aforesaid epoxy resin, as too much epoxy resin may lead to the risque of oozing to the front side of the leather.

Excess of resin used, considering the enormous sizes of the bands of panels, the bad condition of the gilded leather and the increased weight after impregnation would certainly cause difficulties in case the leather should have to be turned over for the removal of superfluous epoxy resin, before it is cured.

Insufficient epoxy resin, on the other hand, would mean the risque of not adhering of the grain side with painting layers to the flesh side.

By conducting experiments we could determine the quantity of impregnating-agent needed. It is not possible to fix a general rule for this, as the quantity depends on the condition of the leather.

The epoxy resin is spread by means of a short, wide-sized brush.

The duration of the hardening-process finally depends on the temperature in the working-room. It is recommendable, therefore, to put some of the epoxy resin used in a beaker to be able to follow the course of the hardening-process..

In the stage when the epoxy resin becomes treacly,the gilded leather should,for better results,be put under pressure.To achieve this we spread a layer of dry sand,10 cm thick,on the back side,over a foil of melinex.But,it is also important not to exceed the weight of the sand,because this would cause the impregnating-agent to be pressed through the crazes in the outer side and thus to discolour the painting.Here too,the carrying out of experiments must preceed. It is also better,after application of the impregnating-agent,to wait some time with pressing the leather with sand,because otherwise the epoxy resin,having a very low viscosity,would be pressed through the leather and do damage to the painted side.
This method is particularly suited for gilded leather,as far as common leather is concerned,because in enclosing the leather the leather fibre,the epoxy resin darkens them,which is esthetically objectionable,while,with gilded leather,this effect,because of the metal foil,varnish and a layer of paint on the front side,is not visible.
The gilded leather was,after its impregnation,treated in the way as discussed in the section on restoration of gilded leather in general.

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CONSERVATION AND RESTORATION OF FUR CLOTHES FROM THE BURIAL PLACE OGLAKHTY (THE KHAKASS AUTONOMOUS REGION), THE TURN OF THE FIRST CENTURY A.D.

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CONSERVATION AND RESTORATION OF FUR CLOTHES FROM THE BURIAL PLACE OGLAKHTY (THE KHAKASS AUTONOMOUS REGION), THE TURN OF THE FIRST CENTURY A.D.

K.F. Nikitina

Abstract

Methods of conservation and restoration of partly deteriorated ancient fur clothes found in dry birch bark burial place Oglakhty are described. The work was carried out in the following order: glueing of the fur, lining of the torn and crumbling edges of the skin tissue, consolidation and fattening of the derm and filling up the losses. Water dispersion of vinyl acetate and 2-ethyl hexyl acrylate copolymer was used for impregnation, glueing and relining.

In September 1969 some excavated materials from the Moscow State University expedition in the Khakass Autonomous Region under the guidance of L.R.Kyzlasov were brought to the State Hermitage (Oglakhty complex).
A man and a woman in fur garments, a chils's skeleton and two leather "dolls" of man's height also dressed in fur clothes lay in a tomb which was a framework made of larch logs covered with several layers of birch bark. The Oglskhty buriels, which according to L.R.Kyzlasov date back to the turn of A.D., were found to be in the conditions of absence of moisture and air access. This favoured the preservation of organic materials: wood, fur, textiles, leather and others. Their physico-chemical properties, however, had undergone considerable changes.

Careful examination of the fur garments undertaken by a commission of archaeologists and restoreres showed that there are considerable losses of both mechanical and biological origin (the result of decomposition or of the rodents and insects activity). Because of the destruction of the epidermis the fur came off the skin tissue which got dry, warped and in some places torn and crumpled; some parts, when slightly rubbed, turn into powder, others disintegrate at the lightest touch. The woman's fur coat can serve as an illustration of the diverse state of preservation of the garments. The coat is made of separate pieces of sheepskin, each measuring 80 x 160 mm. with the fur inside. The fur of the both coat-breasts are preserved rather well. The losses here are due to the action of rodents and insects, mechanical breaks. The losses on the skirt part of the coat and on the back are of different character and origin, resulting from decomposition. Three stages of damages are observed here:

1. The derma lost its elasticity, the hair is preserved, has become wiry, fragile and dull; the epidermis layer which connects the hair with the derma and which undergoes destruction first of all has been fully destroyed with the result that the hair has come off the skin and is lying on the surface.
2. The epidermis is destroyed, the hair cover which came off the derma has dried up, shrivelled, has become stiff and fragile, gets easily broken and is much darker than the derma which is in a good state of preservation.
3. The epidermis is destroyed, the hair cover is lost, the derma is destroyed to such an extent that, when rubbed with the fingers, easily turns into powder. In fact, it is not skin but compacted skin dust.

The diverse states of preservation and all the stages

of destruction are to be seen in all other articles as well: the child's fur coat, breastplate, fur trousers, cap, bag and others.

Though the fur garments were in different states of preservation, sometimes in very poor states, their conservation and restoration was thought possible and necessary. The aim of both of them was to consolidate the coming off fur and to stick up the one already detached, to consolidate the skin tissue, to render it soft, to smooth it down, to reline the parts preserved poorly, to fill up the losses, to restore the shape, size and the cut of the garments.

The conservation of the Oglakhty fur garments was carried out by consolidating it with the polymer water dispersion and the emulsion fattening. The aqueous dispersion of vynyl acetate and 2-ethyl hexite acrylate (VA-2EHA) copolymer was used for impregnation, gluing and relining. This copolymer is plastic (the 2EHA component ensures the intermolecular plastification of the copolymer and its great ageing stability), transparent, possesses good adhesive properties, physically stable, chemically inert. The dispersion penetrates the skin tissue easily, non-toxic and convenient in work.

To soften and fatten the skin, the fattening emulsion and the paste lipodermliquor were applied. The emulsion is composed of the following components: stearine (a chemically stable substance), lanoline (wool-fat), vaseline oil (a petroleum product), cachalot fat alcohol (cetyl), glycerin and triethanolamine (the emulsifying agent - less than 2%). The fattening lipodermlikuor paste contains sulfonated sperm oil, when diluted with water, forms a stable fine emulsion which does not alter the skin tissue colour. It is used in industry for fattening natural fur skins.

Characteristic of the poorly preserved archaeological leather (dry, fragile, loose or thin) is the loss of the tanning matter, dehydration and loss of fat. In over-dried leather the fibres are in a strained deformed state. With the moistening of the collagen the strain disappears, the fibres straighten out. We applied the emulsion technique of fattening when moistening and fattening take place simultaneously. This technique ensures very thin and uniform fat distribution on the surface of the leather fibre structural elements.

The processes of conservation and restoration of all Oglakhty fur garments were carried out in the following sequence. It was thought reasonable to begin with the consolidation of the fur which came off the skin (the consolidation was carried out with the help of a comb with VA-2EHA dispersion using a thin brush) and preliminary relining of the torn and crumbling edges of the skin tissue on tulle. Then pieces of dirt, insect envelopes, rodent excrements and other contaminations were removed from the fur surface by mechanical means. 10% VA-2EHA dispersion was put with a soft brush on the cleaned fur. The dispersion consolidated the epidermis and filled the hair follicles. Treatment of this kind was carried out on small areas. Directly, before the VA-2EHA film got dry, the fattening emulsion was put on the fur surface with a cotton-gauze wad. The substances put on the fur were thoroughly rubbed with the fingers into the skin, massage like. All the above operations were followed by "combing" and drying the fur with a fan against the pile.

The treatment of the articles from the face side was carried out in the following order: at first dry pieces of dirt were removed with a brush and a scalpel, the dust being removed with the help of a vacuum-cleaner

through 2-3 layers of moistened gauze. Then the hard dried dirt was wetted with 2-3% VA-2EHA dispersion with the addition of 4% thymol solution in alcohol using a tough brush, after which the dirt was easily removed with a wad. The cleaned skin was impegnated two or three times with IO-I2% VA-2EHA dispersion, then the fattening emulsion was put. The substances were rubbed into the skin with the fingers, the warped, crumpled and deteriorated areas were flattened out with massage like motions. After such treatment the derma bacame soft and flexible which enabled us, necessary precautions taken, even to smooth out the areas of sharp folds. In case when the smoothing with the help of the fingers was not effective, marble weights and small sand bars were put on the skin. The treatment was carried out on small areas. The weights were put in such a way that in the process of smoothing out the seams should not be crushed flat. To prevent this, some supports were used which helped to carry out the operation preserving the shape of the articles treated.

As a result of all the treatments undertaken, the fur became well consolidated, and the skin so soft and flexible that it was possible to carry out all the restoration processes: to glue up the edges to a narrow canvas strip, to supplement the losses with 2-3 layers of canvas (the first layer is glued up to the edge from the reverse side, the rest are inserted from the face).

In the process of conservation and restoration work it proved possible to reveal some special points of the fur clothes making: the kind of material used, the method of cutting out the details, kinds of the seams; to find out the original size of the garments, their cut and purpose.

78/19/4

REMOVAL OF IRON CONTAMINANTS FROM WET LEATHER USING COMPLEXING AGENTS IN DIPOLAR APROTIC SOLVENTS

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ABSTRACT

Samples of waterlogged leather from the BATAVIA were analysed by X-Ray diffraction and electron microprobe and shown to contain iron, sulphur and oxygen as the major contaminating elements in the form of γ-FeO(OH) and FeS (possibly as pyrrhotite). Hydrolysis experiments under controlled conditions showed that breakdown of such leather depends on the environment while under water and particularly on the stability of that environment.

Attempts to remove all the iron as the thiocyanate complex in dipolar aprotic solvent systems were only partially successful because of dimensional changes produced by the treatment, however, a combined treatment could be possible where all the iron is removed and stability maintained by elimination of rehumidification steps and making use of dipolar aprotic solvent systems throughout.

INTRODUCTION

Leather recovered from shipwrecks invariably contains iron contaminants, in the form of oxides and sulphides, produced by the corrosion of iron ship's fittings and the deposition of iron sulphide by bacteria.

This process is most noticeable where the leather has been attached to iron fittings such as bucket handles, metal scabbards, armour plate, bilge pumps etc.,

Leather, like most organic, polymeric material is rapidly destroyed in the sea by natural processes such as aerobic bacterial decay, and mechanical damage, but when buried in the seabed is immune from such attack and, therefore, its life extended enormously. However, decay is still possible in such unpromising environments through the action of reducing bacteria such as Desulphavibrio sps. which also convert iron, associated with such materials, to iron sulphide. It is, therefore, not surprising to find that leather associated with buried marine wrecks

survives, but is usually more or less heavily contaminated with iron corrosion products, including iron sulphide.

As in most conservation procedures, the removal of contaminants from material before consolidation processes are undertaken is a first priority and the removal of the iron contaminants is no exception - particularly as they can act as a catalyst for the formation of sulphuric acid from Sulphur dioxide (1)(2) present in the atmosphere. Iron compounds are usually removed by dilute solutions of strong acids or by treatment with solutions of complexing agents such as Ethylene diamine tetra acetic acid, disodium salt (E.D.T.A.) or oxalic acid, all of which are used with water as the solvent.

Treatment by the above processes are slow and the acid strength must be kept low to prevent hydrolysis of the collagen (pH stability range 3-5). Water is also not the best of solvents because of solvolysis of the complexing agents, protons and anions produced by dissociation, interfering with the reactions. It was, therefore, decided to investigate possible alternative solvents and complex agents to see if a better system, and possibly even a safer system, could be devised to remove iron from leather.

APPROACH

The solvents most likely to match the above criteria would be those having high dielectric strength, miscibility with water, small hydrogen bonding propensity, and lower solvating power. They must also be the solvents to the complexing ligands and metal complex and, also, solvents in which the ligand and the complex are stable. All of these criteria are met by the dipolar aprotic solvents acetone, methyl cyanide, dimethyl sulphoxide etc., the first two of which are easily obtainable, cheap, and of low viscosity - the latter being an important factor for penetration.

TEST MATERIAL

Leather samples were obtained from material raised from two wrecks off the Western Australian coast; the BATAVIA sunk in 1629, and the EGLINTON sunk in 1852; the former on a reef 50 km from Geraldton, and the latter off Rottnest Island some 20 km due west of Fremantle.

The control specimen for the leather analysis phase was a piece of modern vegetable tanned leather and comparisons were carried out against a piece of 1920's horse harness, neither of which had been subjected to immersion in sea water.

The comparable wreck material was BATAVIA shoe leather, both wet and dry; BATAVIA armour necklet leather (wet) and shoe leather from the EGLINGTON (also wet). All wet samples had been soaked in tap water for periods of at least six months prior to testing and analysis. It would perhaps be pertinent here to explain the term "armour necklet leather." This was leather in the form of thin strips some 12 mm wide and 2 mm thick, punctured with 3 mm diameter holes at regular intervals along its length, derived from armour upper chest and back guards, which were used to protect the thoracic region of the chest and/or back. The leather was rivetted to the rear of the armour plates to act as a protection, for the wearer, from the metal. In a large number of cases the centre area of the leather had been lost by decay but the rivetted edge of the leather had been retained, possibly because of the high iron content produced by the corrosion products from the armour plates. These pieces were, therefore, a good test of any iron removal process.

EXPERIMENTAL

Electron micrographic studies of BATAVIA armour necklet leather, and samples from the horse harness and control specimen showed little structural difference apart from closer packing of the dry horse harness, collagen fibres and the apparently shorter fibre structures of the BATAVIA and EGLINGTON leathers.

Controlled hydrolysis, however, showed considerable differences in the various leather samples - in this case samples of horse harness, wet BATAVIA shoe leather, dry BATAVIA shoe heel and wet EGLINGTON shoe leather. The dry BATAVIA shoe heel leather was obtained from a block of concretion which had been allowed to dry out for about two years before being broken open.

The results of this series of experiments is given in TABLE I.

TABLE I

CONTROLLED HYDROLYSIS OF LEATHER OF VARYING AGES AND ENVIRONMENTS

Leather Sample	% Hydrolysed w/w	% Residue
Control (modern)	36.7	63.3
Horse Harness (1920's)	34.5	65.5
Wet Batavia shoe	63.3	36.7
Dry Batavia shoe	73.1	26.9
Wet Eglington shoe	81.9	18.1

Each sample was first dewatered with acetone, dried and then weighed. The weighed sample was then refluxed for four hours with 25 mls of 5 mol/l Hydrochloric Acid and the weight of residue determined after washing and drying. Both the control and horse harness samples showed a loss of approximately one third of their weight, where as the BATAVIA samples had lost approximately two thirds of their weight and the EGLINGTON sample even more, at 80%.

All the samples were taken from material which was apparently sound and no outer surfaces were used, only inner core material, to eliminate iron contamination errors and excessive corrosion areas.

These results would seem to indicate that the collagen in leather from wrecks is far from sound in condition and that this condition depends rather on the environment and less on the age of the material after burial on wreck sites or the age of the wrecks. An interesting confirmation of these conclusions is the analysis of the same materials for their fat content, the results of which are given in Table II.

TABLE II

FAT CONTENT OF LEATHER OF VARYING AGES AND ENVIRONMENTS

Leather Sample	Fat Content (ASTM) (%w/w)
Control	4.9
Horse Harness	10.1
Wet Batavia shoe	0.8
Dry Batavia shoe	5.2
Wet Eglington shoe	0.6

The high fat content for the horse harness is obviously because of the use of dubbin to keep the leather flexible during its working life. The BATAVIA leather which was trapped in concretion has lost less oil/fat than similar material open to chemical and bacterial decay.

Analysis of washed necklet armour leather for mineral content by both wet chemical and electron microprobe (EMP) methods were carried out. The results of these analyses are given in Table III.

TABLE III

ANALYSIS OF MINERAL CONTAMINANTS - ELEMENTAL ANALYSIS

Wet Chemical		Electron microprobe (SILI detector)	
Cation or Anion	Concentration of Ion	Element	Concentration of Element
Fe^{+++}	++++	Fe	++++
Cu^{++}	+	Cu	++
Cl^{-}	+	Ca	+
$SO_4^{=}$	+++	S	+++
Na^{+}	+	Al	++
K^{+}	+	Mg	+

Quantitative analysis of this same material was carried out, for the major elements, using Atomic absorption spectrophotometry (A.A.S.) and E.M.P. methods.

Surface scrapings from the necklet leather had an iron content of 25.5%; a sulphide content of 7.8% and a chloride content of 0.7%. The core leather from the same sample gave results of 13.2, 6.6 and negligible per cent for iron, sulphide and chloride respectively - showing that a quite high concentration of iron was present in the leather matrix.

The iron content of the control leather was found to be 1.7%; X-Ray diffraction analysis showed the iron to be in two major crystalline forms. On the surface the iron was present as γ-FeO(OH)(Lepidocrocite) and in the leather matrix as γ-Fe_2O_3, although the latter may be derived from the former during the drying process. The sulphide present was not detected as an iron sulphide because of the swamping effect of the iron oxide.

E.M.P. quantitative analysis confirmed the presence of both γ-FeO(OH) and γ-Fe_2O_3 and from sulphide content - excess iron content ratio, the sulphide was considered to be present as iron sulphide, probably in the form of pyrrhotite $Fe_{1-x}S$ where $2 > x > 0$ or bacterially deposited sulphide(3).

Tests to determine the best solvent system for removal of iron, using the thiocyanate ion in acid medium as the complexing agent, indicated a mixture of Acetonitrile (CH_3CN)(Methyl cyanide), Acetone ($(CH_3)_2CO$) and water in the ratio 5:4:1 respectively. This system lowered the iron content in pieces of necklet armour from 20.4 to 5.8% over a period of five days.

X-Ray diffraction studies of the treated leather showed a considerable drop in line intensity and E.M.P. analysis showed a drop in iron content but not in sulphide, indicating the residual iron to be the "pyrrhotite" originally determined. The treatment was monitored through the red colour the solution develops due to the formation of the soluble iron complex hexa thiocyanato ferrate III, and the solution changed when this colour had reached maximum intensity. When no further colour increase occurred the leather was removed, washed with acetone, dried and the chemical and physical analysis undertaken.

To remove the iron sulphide a complexing system, normally used industrially for copper recovery, was tried. This process is normally used in reverse where the copper is recovered and the pyrrite dissolved in the solvent.

The process devised was to place the leather sample in an aqueous methyl cyanide solution containing copper ions and 0.01 mol/l acid and allowing it to soak in the medium for one week. After this time the sample was removed and analysed for its iron content. The new level of iron was found to be 4% lower than the original and represented a 20% decrease in total iron content. Considering the original sulphide represented 28% of the iron by difference and assuming the original leather contained 1.7% iron as did the control, probably as iron complexed with the collagen, then this 20% drop in iron content probably represents all the iron present as sulphide, ie the methyl cyanide process removes all the iron sulphide without removing the iron oxide or collagen complexed iron.

Studies of dimensional changes produced by treatment of iron contaminated water-logged leather using dipolar aprotic/aqueous systems with various organic complexing agents and also thiocyanate irons with inorganic acid were undertaken.

Samples of necklet leather were marked with metal pins, as also was a sample of control leather and the dimensions between the pins determined.

Pairs of necklet leather pieces were treated with either a solution of ammonium oxalate in methyl cyanide-water-acetone (16:4:1) or citric acid in methyl cyanide-water-acetone (8:1:1) for one week, and then the sample equalibrated with water at 100% RH, and the dimensions again measured.

The necklet pieces were then transferred to 1.0% w/v ammonium thiocyanate in either acetone-water (4:1) or methyl cyanide-acetone-water (6:3:1) mixtures, both 0.01 mol/l in sulphuric acid. The pieces were selected so that one from each of the pretreatment solutions was treated in each of the thiocyanate solvent systems as indicated in Table IV.

TABLE IV

THE STABILITY OF LEATHER AFTER IRON REMOVAL WITH APROTIC SOLVENTS

Sample	Organic Complexing Agent		SCN$^-$ Solvent System	
	Citric	Oxalate	CH_3CN	$(CH_3)_2CO$
Control	-	-	-	-
I	X		X	
II	X			X
III		X	X	
IV		X		X

After one week in the appropriate solution the samples were removed, washed in fresh solution, equalibrated with a 100%RH atmosphere and the dimensions redetermined. Samples of each piece of leather were taken, denatured in acetone, dried at 120°C for two hours and then the iron content determined. These results are given in Table V.

TABLE V

IRON CONTENT AND DIMENSIONAL CHANGES OF TREATED LEATHER SAMPLES I-IV

Sample	I	II	III	IV	Control
% Fe .	9.1	13.1	1.8	5.4	-
Dimensional Changes(%)	-1.6	-0.2	-19.77	-27.3	+0.47

From these results it will be noted that the greatest iron loss produces the greatest dimensional change (20-30%) and as would be expected, acetone, a good dehydrating agent, has a greater effect on shrinkage than methyl cyanide. The degree of degradation of the leather will also be a controlling factor in dimensional stability after the supporting effect of iron corrosion products is removed. It is, therefore, not surprising to find the highest iron residue produces the smallest dimensional change, particularly if methyl cyanide is used as the complexing solvent.

Considering the ease with which the BATAVIA shoe leather was hydrolysed and in view of the fact that the corrosion of iron produces a lowering of pH locally (4)(5), then it would not be surprising that the necklet leather should be more corroded than the shoe leather tested for hydrolysis and, therefore, even more liable to shrinkage.

CONCLUSIONS

The use of complexing agents in dipolar aprotic solvents is a successful way to remove iron oxide and sulphide contaminants from water-logged leather but has the disadvantage of causing considerable shrinkage - although some of this shrinkage may be due to the rehumidification procedure used in the tests. It may well be possible to remove the iron as above and then consolidate with a suitable consolidant, such as P.E.G. in a dipolar aprotic solvent or in even less degraded leather, lubricate with neatsfoot oil in such solvents(6).

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EASEL PAINTINGS

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Programme 1975-1978

1. Stabilité des couleurs utilisées à la restauration (Callede).
2. Matériaux et techniques utilisés dans la peinture italienne du XIVème au XVIème (Delbourgo).
3. Technical studies on East Asian paintings (Winter).
4. Further investigation in the alteration on green paint-layer. Ground-layers of baroque paintings (Mairinger).
5. Investigation on original geographical and geological sources of pigments (Grissom).
6. Further investigation in brown discolouration on green paint (Groen).
7. Further aspects of materials and techniques of Tintoretto (Plesters).
8. Les effets des solvants sur les couches picturales (Dauchot-Dehon).

78/20/1

ETUDE COLORIMETRIQUE DU VIEILLISSEMENT DES COULEURS UTILISEES EN RESTAURATION

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ETUDE COLORIMETRIQUE DU VIEILLISSEMENT DES COULEURS UTILISEES EN RESTAURATION

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Les couleurs commercialisées employées en restauration vieillissent différemment dans le temps. Afin de sélectionner des produits d'une stabilité maximale, le L.R.M.H. a testé des éprouvettes de différentes marques dans chaque couleur à l'aide d'un colorimètre MOMCOLOR (usine d'optique hongroise, Budapest). Les résultats des mesures sont donnés suivant le système C.I.E. (Commission Internationale de l'Eclairage) et leur interprétation a été traitée par informatique.

METHODOLOGIE

La méthodologie et les appareils utilisés jouent un rôle très important en colorimétrie, car il s'agit d'éviter la subjectivité propre aux méthodes comparatives (type code des couleurs). Nos mesures et les calculs en résultant pour l'exploitation ont été faits dans le système international C.I.E. en coordonnée x, y, Y. Nous donnons ici un bref rappel de ce système :

Le système C.I.E. de mesures de couleurs (1)

Toute couleur peut être définie par une combinaison de 3 couleurs fondamentales. Dans le système considéré, celles-ci ne sont pas des couleurs réelles, mais correspondent à des stimulus définis artificiellement pour obtenir une représentation graphique de l'espace des couleurs répondant à certaines conditions pratiques. Ces 3 primaires sont représentées par les lettres X, Y, Z, et une couleur quelconque peut être définie symboliquement par l'équation :

$$xX + yY + zZ = S, \text{ avec } x + y + z = 1$$

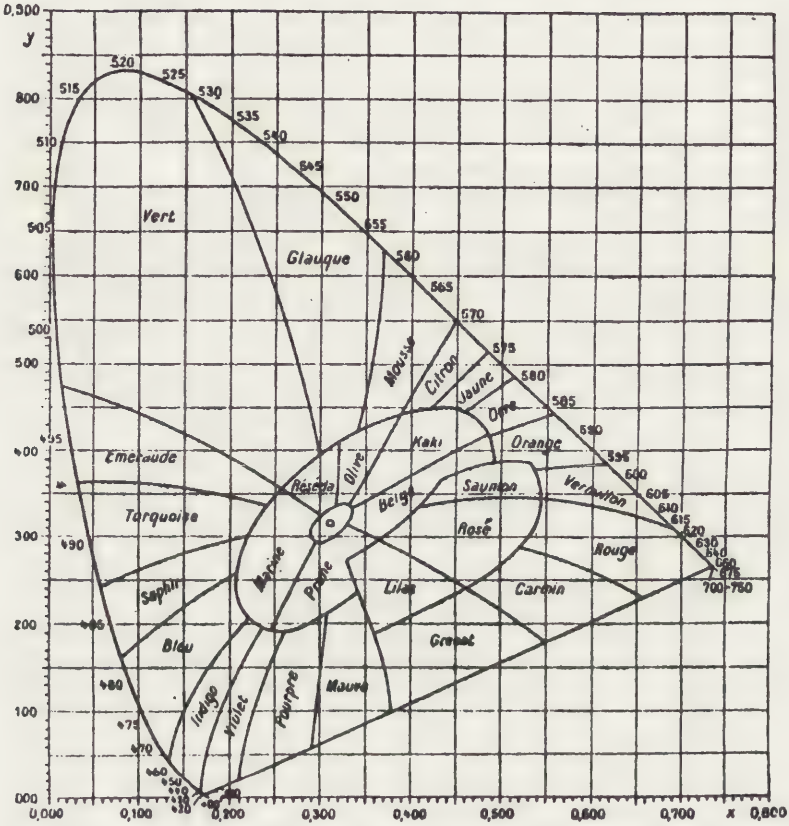


FIG. 1. — Désignation des couleurs dans le diagramme trichromatique.

On obtient ainsi une représentation graphique plane de l'espace des couleurs, que l'on donne fig. 1. Les points situés sur la courbe représentent des longueurs d'onde pures. Si l'on part d'un de ces points et que l'on se dirige vers le point W (incolore), on a des couleurs non saturées, de plus en plus délavées de blanc. Les deux coordonnées x et y suffisent donc à définir une couleur en teinte et saturation (ce qui correspond en gros aux notions H et C du code Munsell). Quant à la luminosité (ou valeur), qui permet de situer une couleur par rapport à l'échelle des gris allant du noir pur au blanc pur, elle est représentée par la coordonnée Y, comprise entre 0 et 100 %.

Pour les expériences décrites ici, on peut donc comparer de façon rigoureuse une couleur avant et après vieillissement : la comparaison des coordonnées x et y permettra de faire figurer deux points sur le diagramme des couleurs, donc de voir dans quel sens s'est déplacé le point figuratif : blanchissement, variation de la teinte, etc... La variation de la coordonnée Y permet d'apprécier l'évolution de la luminosité de la couleur en question. Nous reviendrons plus loin sur ces appréciations et leur marge d'erreur.

Matériel utilisé

L'appareil employé pour les mesures est un MOMCOLOR (2, 3), colorimètre tristimulus ; les excitations primaires X, Y, Z sont obtenues par un système de filtres. La tête de lecture comporte un illuminant C (lumière du jour). Une fois étalonnée la température de couleur à l'aide de l'étalon blanc, on effectue la série des mesures dans la couleur considérée (étalon de la couleur donnée). Les mesures sont entièrement automatiques ; pour chaque filtre, après un temps de stabilisation, la valeur affichée pour la mesure de X, Y ou Z est envoyée à une calculatrice spécialement programmée, qui calcule et imprime aussitôt les valeurs de z, y, Y, ainsi que la différence de couleur Δ E (formule d'Adams Nickerson) (4) par rapport à la référence choisie. Ceci pour toute une série d'échantillons. On a effectué 3 mesures pour chaque échantillons, et pour la comparaison des résultats, on a pris les valeurs moyennes de x, y, Y.

Exploitation des résultats

La complexité des calculs en colorimétrie et le nombre important des mesures rendaient pratiquement indispensable l'utilisation de l'informatique pour parvenir à une exploitation pratique des résultats. Aussi a-t-on mis au point un programme pour un petit ordinateur (H.P. 9825), qui a per-

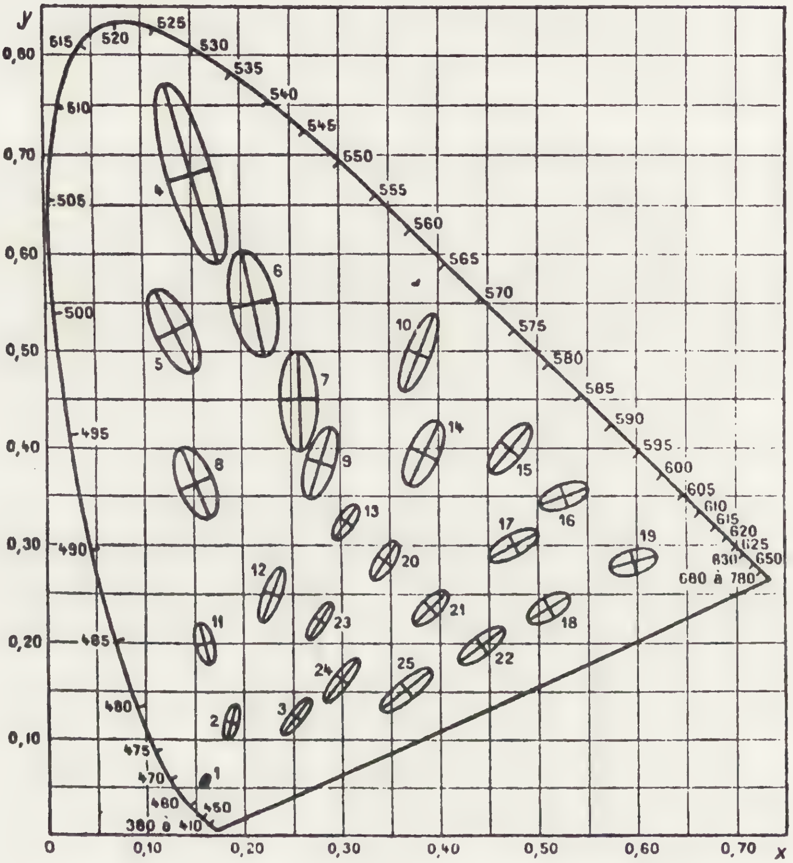


FIG. 2 — Seuils différentiels à luminance constante, des couleurs, schématisées dans le système C.I.E. par les ellipses de Mac Adam.

Les centres sont placés correctement dans le diagramme chromatique de la C.I.E., mais les dimensions des ellipses sont multipliées par 10.

mis d'une part de visualiser les résultats pour chaque couleur, et d'apprécier ainsi sa variation, d'autre part pour tenter de synthétiser les résultats.

Appréciation des variations

La question qui se posait, pour apprécier objectivement la variation au vieillissement d'une couleur donnée, était évidemment de savoir à partir de quelles différences des coordonnées x et y, on estime qu'il y a une variation appréciable ; en d'autres termes, à partir de quelle distance entre les points figuratifs, on peut la considérer comme appréciable. Cette question est compliquée par le fait que l'espace plan x, y n'est pas homogène, en raison du système mathématique de représentation et aussi de la sensibilité de l'oeil qui varie selon la teinte observée (il s'agit bien entendu de l'oeil dit "normal", parfaitement défini). Autrement dit, en un point donné du diagramme, 2 couleurs représentées par 2 points à une certaine distance paraîtront identiques à l'oeil, alors qu'en un autre endroit la même distance correspondra à 2 teintes paraissant différentes.

Les études sur cette question ont montré qu'on peut admettre que pour un point donné, la zone d'erreur, c'est-à-dire la zone dans laquelle l'oeil ne peut pas apprécier la variation de couleur, est représentée par une ellipse appelée ellipse de Mac Adam. Les dimensions et l'orientation de chaque ellipse dépendent des coordonnées de son centre. Comme on peut le voir fig. 2, les zones de tolérance sont beaucoup plus grandes dans la zone des verts que dans celle des bleus.

Le principe de notre méthode était donc le suivant :

- Pour chaque échantillon, on effectue 3 mesures avant vieillissement et 3 mesures après vieillissement
- on réalise ensuite la moyenne de ces 3 mesures, ce qui donne une valeur moyenne pour x, y, Y avant et après : x', y', Y'
- on construit l'ellipse de tolérance de centre x, y, Y
- on place ensuite sur le diagramme le point de coordonnées x', y', Y'.

Si ce point tombe à l'intérieur de l'ellipse, on considère qu'il n'y a pas de variation notable. S'il tombe à l'extérieur, on considère que la couleur a varié de façon sensible à l'oeil. On peut alors étudier dans quelle direction se fait cette variation.

Comme on l'a dit plus haut, étant donné le grand nombre de mesures, il était nécessaire d'utiliser un ordinateur. Le

programme permet d'introduire en mémoire toutes les mesures pour une série de 25 échantillons, et l'appareil donne ensuite sur l'imprimante le tableau des valeurs avant et après vieillissement, les différences, et trace le diagramme avec le point initial, l'ellipse de tolérance et le point final. Le résultat de la variation de couleur apparaît ainsi directement sur le diagramme.

APPLICATION

Principe de l'étude

Nous avons présenté, lors de la 4e réunion triennale à Venise en 1975, une étude intitulée "stabilité des couleurs utilisées en restauration (5) : pigments bleus". La méthode adoptée présentait deux inconvénients. Tout d'abord la comparaison des pigments avant et après vieillissement était faite à partir du code Munsell, les appréciations des nuances étaient donc subjectives, puisque dépendant de l'oeil de l'observateur et de la température de couleur de la lumière ambiante. De plus, les couleurs n'avaient été testées qu'en pâte, ce qui gênait quelquefois l'appréciationtion des variations.

Pour pallier à ces imprécisions, le L.R.M.H. s'est équipé d'un colorimètre MOMCOLOR et les couleurs ont été testées en pâte et en glacis posés sur un gesso composé de plâtre mort et de colle animale.

Méthode de vieillissement

Les deux types suivants de vieillissement ont été pratiqués :

- Vieillissement aux ultraviolets dans une enceinte climatique Karl Weiss munie de 6 tubes Sylvania/lifeline type F 20 T 12/CW lumière froide blanche et de 2 tubes Sylvania type F 20 T 12/BLB lumière noire-bleue.
  Les éprouvettes ont été soumises aux radiations pendant 400 h à une température constante de 20°C et une humidité relative de 55 %.

- Vieillissement climatique dans la même enceinte. Les éprouvettes ont subi 40 cycles se décomposant comme suit :
  . 6 heures : température 3°C, humidité relative 90 %
  . 6 heures : température 40°C, humidité relative 12 %.
  La variation de 3°C à 40°C provoquant une condensation (humidité relative 100 % pendant 1/4 d'heure environ).

Dans les deux cas un enregistreur contrôlait la régularité des essais. Afin de se rapprocher au maximum de la réalité, nous avons adopté des cycles correspondant à un vieillissement lent en banissant les écarts de température trop importants et l'emploi de lampe à ultraviolets trop puissante (par exemple lampe à Xénon).

Ces tests ont pour but de connaître, d'une part l'incidence des ultraviolets sur la couleur, d'autre part de vérifier la sensibilité possible de celle-ci à l'humidité. Il est en effet possible qu'une couleur très stable à la lumière ne le soit pas en milieu humide, ce qui déconseillerait son emploi pour les oeuvres placées dans des églises, par exemple les peintures murales, les bois polychromes.

Les résultats obtenus ne sont valables que par comparaison entre eux et ne peuvent, en aucun cas, être interprêtés comme équivalents à un vieillissement de x nombre d'années.

Produits testés

Après enquête auprès des restaurateurs, notre choix s'est porté sur les teintes les plus couramment employées dans les marques suivantes :

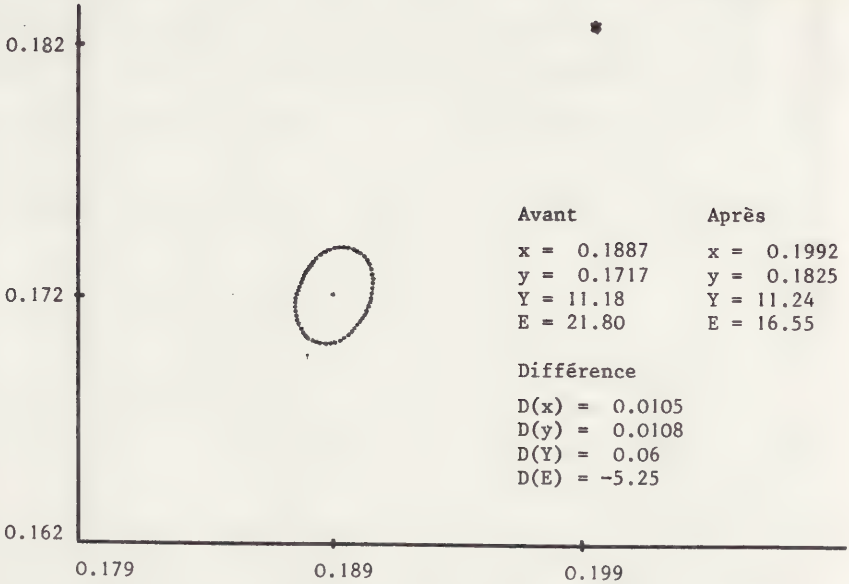
- FLASH de Lefranc Bourgeois
- MUZII de Lefranc Bourgeois
- PLAKA de Pelikan
- ACRYLIC de Lascaux
- CRYLA de Rowney
- Couleurs pour restauration de chez Maimerie.

Résultats

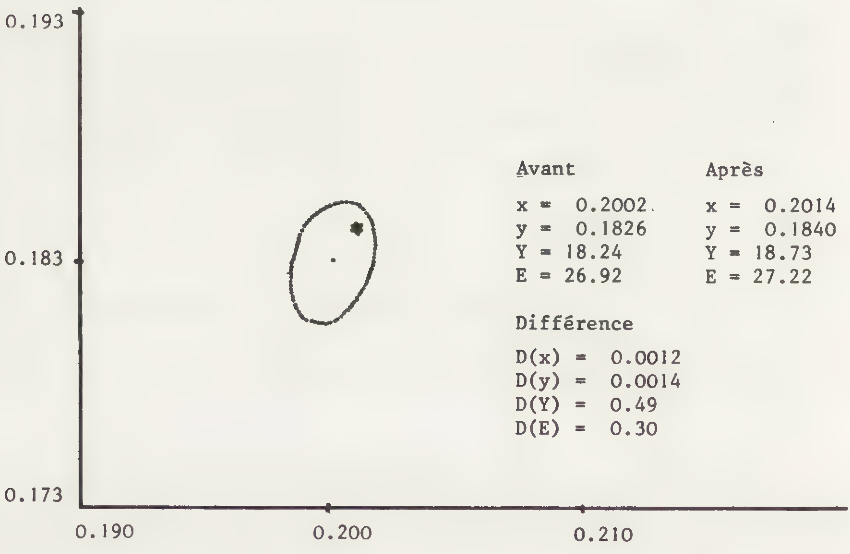
Nos études portent sur :

- la mesure des coordonnées trichromatiques de chaque couleur prise séparément
- la comparaison des mêmes teintes dans les différentes marques(par exemple tous les bleus outremer)
- la comparaison de l'influence des différents liants sur chaque couleur.

Nous présentons, ci-après à titre d'exemple, 2 graphiques correspondant à 2 bleus de Cobalt, l'un de marque MUZII, l'autre de chez LASCAUX. Lorsque le point représentant la couleur après vieillissement se trouve à l'intérieur de l'ellipse de Mac Adam(zone dans laquelle l'oeil ne perçoit pas de différence),la couleur est considérée comme stable. Par contre, si ce point est situé en dehors de l'ellipse, la couleur a varié.



Echantillon : Bleu de Cobalt Muzii en glacis (✱) *après vieillissement*



Echantillon : Bleu de Cobalt Lascaux en glacis (✱) *après vieillissement*

Les résultats des expériences sont actuellement en cours de dépouillement. Leur interprétation sera présentée lors de la réunion de Zagreb.

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78/20/2

DIFFERENTIAL THERMAL ANALYSIS OF PAINT SAMPLES

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DIFFERENTIAL THERMAL ANALYSIS OF PAINT SAMPLES

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Summary

Differential thermal analysis (DTA) is a routine method in industrial laboratories for the characterization of organic and inorganic materials. It is also used for studies of the ageing properties of materials, especially of synthetic polymers. In 1976 the Doerner-Institut started a research project on the possibilities of this method in the field of archaeometry. The materials included in this study are painting materials, waxes, resins, adhesives, organic conservation materials and others.
As a result of the first year it can be said that DTA is a practicable method for archaeometric research. The thermoanalytical curves received from samples of oil paintings heated under oxygen show a strong dependence of the age of the sample within a range of about 120 years. Characteristic for oil-media without additives are two exothermal reactions, one at about 300°C, the other at about 400°C. The ratio of these two reactions depends linearly from the logarithm of the age of the painting. This gives the possibility to identify recent forgeries of oil paintings, even if they are painted with "historical" pigments (e.g. lead-tin-yellow) as it happened in the last years in Germany.

Introduction

Differential thermal analysis (DTA) is one of the major methods in the great field of thermal analysis (other methods e.g. thermogravimetry, differential calorimetry, effluence analysis). In differential thermal analysis a sample and inert reference material are heated or cooled linearly in a special furnace. The measured variable is the temperature-difference between sample and reference. Any phenomenon that produces an enthalpic change or a change in heat capacity (second-order transitions) can be detected by DTA (e.g. glass transition, fusion, evaporation, dehydration, oxidative degradation, oxidation and reduction in gaseous atmosphere, polymerization). Since binding media analysis is still in the developing stage and the study of restoration materials (especially synthetic materials) becomes more and more necessary we decided to start a research project using DTA as analytical method.

DTA of painting materials

In the first year we concentrated on paintings and painting materials. In a first step we studied the pure materials (pigments, oils, different proteins, waxes, resins and others). The size of the samples varies between 0.2 and 0.9 mg, the heating rate was 5°/min. We found it necessary to measure the different materials one times under nitrogen and one times under oxygen.
If the sample is too small for two thermogramms it is better to study it under oxygen. Under these conditions it is possible to identify a great variety of the pure materials. In mixtures of different pigments together with different binding media the interpretation becomes difficult. In most cases one can neglect the influence of the pigments on the thermal behaviour of the sample. The thermogramm depends on the composition of the binding medium. Since the final thermogramm of a mixture of different binding media is not the sum of the thermogramms of the single components it is necessary to prepare an atlas of thermoanalytical curves of binding media different in composition and age. For these measurements we use paint-samples prepared for technical experiments at the Doerner-Institut in the years between 1920 and 1950.
Parallel to the preparation of the DTA-atlas we study samples taken from dated paintings of different age. These samples are also studied by infraredspectrography, staining techniques, pigment analysis and microchemical methods. Thermogramms received from paint-samples of different composition show a strong dependence from the type of the binding medium (oils, proteins, tempera) and are sensitive to additives.
Thermogramms of oil-media additionally depend on the age of the sample. Under oxygen one normally gets two exothermal reactions, one at about 300°C the other at about 400°C. The relative intensity of both reactions depends upon the age of the painting. A sample older than about 150 years gives only a very small reaction at 300°C and a very strong reaction at 400°C. A more recent sample gives a reverse thermogramm. The ratio of the intensities of those two reactions depends linearly on the logarithm of the age of the sample.
There are some facts to pay attention to while interpretating the thermogramms of paint-samples:
1) The shape of the thermoanalytical curve reflects in a very sensitive way the presence of additives in the binding medium. If there are unusual peaks or shoulders one must be careful with the quantitative interpretation of the thermogramm.

2) We made the experience that dark samples, specially dark brown samples from the background of a painting, give the best results as far as age-determination is concerned.
3) It is necessary to study at least two or three samples of one painting in order to avoid misinterpretations.
4) The samples should not contain portions of the ground or the varnish, even if its an oil-ground. The samples should only consist of material from the top layer of the painting.

Discussion

The described method provides a good possibility to detect recent forgeries of oil paintings. The importance of such a method turned up in the last years, when forgeries and imitations were sold in Germany which were made with historical pigments (lead-tin-yellow, azurite, verdigris and others).
At the present time it is not quite certain whether this method can be used for a rough dating of paintings of the past 100 years, because we still have not enough reference material to evaluate the error of DTA-dating. Besides the determination of the age of oil paintings differential thermal analysis gives a good possibility to detect binding-media-mixtures and to study technical characteristics of different painters.

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ADVANCES IN THE INFRARED SPECTROSCOPIC EXAMINATION OF PIGMENTS

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ADVANCES IN THE INFRARED SPECTROSCOPIC EXAMINATION OF PIGMENTS

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Abstract

High resolution Fourier transform infrared spectroscopy was used to identify an alizarin lake (Forbes 6.03.36) as a Ca-Al alizarin complex on an alumina lake. The inadequacy of existing collections of infrared spectra of pigments are noted.

Infrared spectroscopy may be used in two general ways to examine pigments. The first and apparently simpler task is to characterize a pigment, i.e., to obtain a spectral signature which is characteristic of the material. As the spectral signature of a particular substance is unique, infrared spectroscopy can be used to characterize or "fingerprint" pigments even if their compositions are totally unknown. The simplicity of this task is, however, deceptive because fingerprinting can only be done if the spectral signatures are detailed enough. For example, Fig.1 shows the spectra of three different anthraquinoid lakes. In the region below 2000 cm^{-1}, the top spectrum differs considerably from the others, and it is readily apparent that pigment 6.03.36 has a substantially different composition than the other two pigments. The spectra of the latter, however, show the same general outline; they are differentiated by the minor spectral features. If these are not recorded precisely -- or, as is usually the case, if it is not possible to record them because the instrumentation is not adequate -- the substances cannot be differentiated.

The second and more involved task is to identify or analyze pigments in terms of chemical composition. For example, during our as-yet incomplete study of madder lakes we recorded the spectra of Fig.2. Trace A is a segment of the top spectrum of Fig.1, scale-expanded so

that the spectral detail stands out more clearly. Trace B is a segment of the spectrum of pure Ca-Al-alizarin complex, and trace C is that of that complex deposited on the surface of alumina. Examination of the three spectra shows that there are substantial similarities; the band positions are identical, and differences arise mainly from variations in band intensities. To bring this out more clearly, spectrum A has been superimposed on spectrum C (the broken line). Consequently, because the spectra are so similar, one may conclude that the pigment 6.03.36 consists predominantly of an alumina-based alizarin lake. More specifically, the pigment is predominantly the Ca-Al alizarin complex on an alumina lake.

In order to be able to make such a specific assignment it was again necessary to have spectra of a quality superior to that customarily obtained. This strict requirement can be appreciated by comparing spectra C and D.

Trace D is a segment of the spectrum of a pigment prepared by depositing the K-Al-alizarin complex on an alumina base. Trace C has been superimposed on trace D to permit easier comparison. It is obvious that the spectra of the two complexes bear great similarities, but also that there are small yet significant differences in band positions. (Spectra of other alizarin-metal complexes show similar but significant differences.) If such decisive differences are not observable, as is usually the case, spectra C and D become identical and an identification cannot be made. In fact, the spectra of various alizarin complexes are identical when recorded by conventional spectrometers under the conditions usually employed.

It is thus apparent that considerable progress can be made toward the infrared spectroscopic examination of pigments (and other substances, of course) if spectra are recorded with sufficient resolution and overall precision. As we have pointed out elsewhere, the Fourier transform spectrometer is particularly well suited to these tasks (1,2). Small, inexpensive laboratory instruments do not have the necessary capabilities, and even most of the "research quality" spectrometers of earlier decades were and are incapable of yielding spectra of the high quality required. It is thus also apparent that many and perhaps most of the spectra of the normally complex mixtures used in the fine arts which have been recorded previously are inadequate and usable only for uncomplicated work. Consequently, published collections of spectra are obsolescent. It will be necessary to establish new ones produced under conditions of uniform high resolution throughout the entire spectral range.

Acknowledgment

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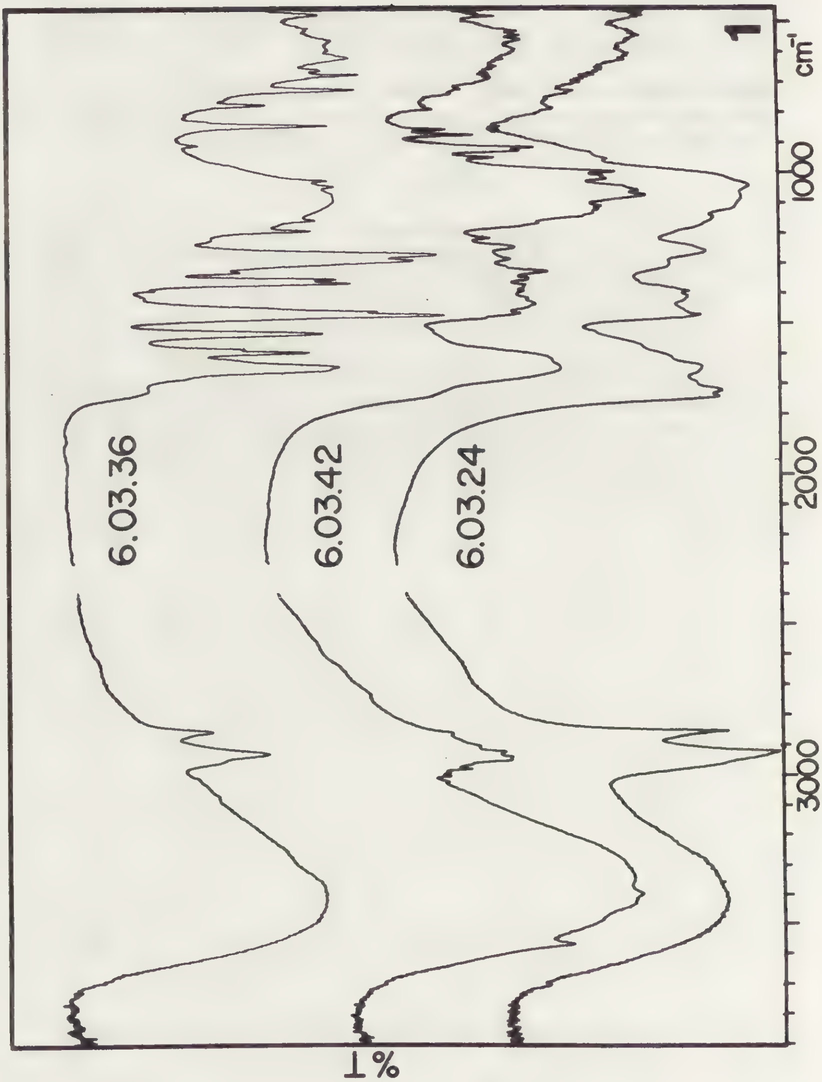
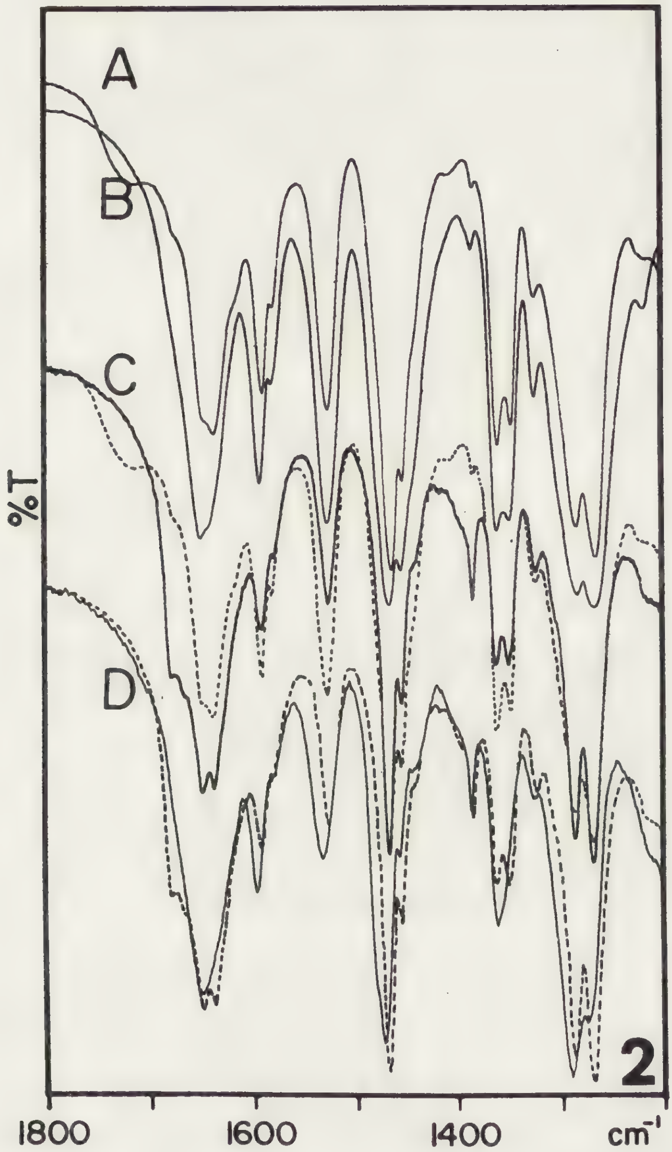
Figures

Fig. 1. Infrared spectra of anthraquinoid lakes. The number by each trace is the Forbes number. 6.03.36, Alizarin lake, Stanley & Doggett, 1924; 6.03.42, Madder, T. Hollis; 6.03.24, Indian lake, Robertson 120. Spectra of KBr pellets were recorded with a Fourier transform spectrometer (1,2). The resolution is 2 cm^{-1}, constant through the frequency range.

Fig. 2. Segments of spectra. A: scale-expanded segment of the top spectrum of Figure 1., of pigment 6.03.36; B: Ca-Al-alizarin complex; C: pigment prepared by depositing the Ca-Al-alizarin complex on alumina; D: pigment prepared by depositing K-Al-alizarin complex on alumina.


1
cm⁻¹
1000
2000
3000
6.03.36
6.03.42
6.03.24
%T


A
B
C
D
%T
1800
1600
1400
cm⁻¹
2

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QUELQUES DECOUVERTES RECENTES SUR LA TECHNIQUE PICTURALE DU XVIIIème SIECLE EN RUSSIE

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QUELQUES DECOUVERTES RECENTES SUR LA TECHNIQUE PICTURALE DU XVIIIe SIECLE EN RUSSIE

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Les études contemporaines sur la technique picturale en Russie sont très peu nombreuses.

On trouvera comme point de départ à ces recherches les travaux de A.N.Loujetskaïa, ainsi que ceux de M.N. Moleva et E.Belioutine, publiés dans les années 60. On peut exposer de la manière suivante leur point de vue sur la technique picturale en Russie au XVIIIème siecle.

Pratiquement la composition de la couche de peintre ne change pas durant tout le XVIIIème siècle; celle-ci appliquée en trois étapes successives: une couche sous-jacente colorée, le dessin des contours et la couche de surface avec les glacis. C'est l'enduit qui a le plus évolué. Au début du XVIIIème siècle il n'était formé que d'une seule couche de couleur, dans la seconde moitié du siècle on trouve deux couches. Lorsqu'il n'y avait qu'une seule couche, elle était brun-rouge. Quand il s'agissait de deux couches, l'inférieure tirait aussi sur le rouge, la supérieure était claire, tirant sur le blanc. On suppose que les enduits à une seule couche n'ont plus été utilisés aux environs des années 60. Aussi la nature de l'enduit d'un tableau est-elle souvent presque l'unique critère pour le dater.

Cependant, la pratique a montré que sur une telle base, l'expertise des oeuvres du XVIIIe siècle ne donnait pas des résultats fiables.

Les recherches pratiquées par la section d'expertise de notre centre de restauration ont modifié quelque peu et ont aussi précisé les notions traditionnelles que l'on avait sur la technique picturale en Russie au XVIII siècle. Elles ont aussi apporté des critères complémentaires pour la datation des oeuvres.

Le spécialiste, étudiant l'art russe du XVIIIe siècle, se heurte à de nombreuses difficultés dues au fait que les oeuvres à examiner sont disséminées dans de nombreux musées. Les expositions de ces dernières années, consacrées surtout au portrait au XVIIIe siècle, ont considérablement facilité notre tâche. Grâce à elles nous avons pu recueillir un vaste matériel relatif à la technique picturale du premier tiers du XVIIIe siècle et augmenter nos connaissances sur celle de la deuxième moitié du même siècle. Il convient de noter que la peinture des années 30 et 40 reste jusqu'à présent une tache blanche non seulement sur le plan de la technique picturale mais sur le plan de l'histoire de l'art russe.

Le matériel proposé ici provient de l'examen de plusieurs dizaines d'oeuvres picturales. Les recherches ont été menées I) sur les enduits 2) sur la couche colorée.

Nous avons surtout étudié les portraits dans la mesure où c'était le genre dominant de l'époque. Nous avons examiné les toiles non seulement de peintres russes, mais également de maîtres étrangers ayant travaillé en Russie au XVIIIe siècle. Il convient de noter tout de suite qu'il n'y a pas de différence sensible entre la technique des artistes russes et celle des artistes occidentaux.

Commençons par les enduits.

Dans le premier tiers du XVIIIe siècle, ils sont généralement formés d'une seule couche brun-rouge de différentes nuances, conformément au point de vue que nous avions jusqu'alors. Ce qui est nouveau, c'est la mise en évidence d'enduits à deux couches dans les oeuvres du début du XVIIIe siècle. Les deux couches sont brun rouge et ne se distinguent entre elles que par une nuance de ton.

Nous avons pu aussi préciser la composition qualitative des enduits. Pour la première fois, il a pu être établi que l'on utilisait le cinabre, sulfate de mercure Hg S, dans la composition des enduits. La base de l'enduit était constituée de terres comme l'ocre ou la terre bolaire. Le cinabre a été découvert grâce à l'analyse de lames microscopiques avec un microscope Mim-8, par un grossissement de 240 fois.

Les particules de cinabre ont une forme et un éclat caractéristiques, rappelant ceux de l'aventurine et c'est pourquoi on les distingue très bien même si elles sont mêlées à d'autres couleurs proches. Quant on regarde la lame, on a l'impression que le cinabre y est mélangé à l'ocre (ou à la terre bolaire) dans les mêmes proportions. Mais cette impression est fausse. Le mélange contient si peu de cinabre qu'on ne peut pas le détecter par l'analyse chimique. C'est pourquoi sa présence dans les enduits du début du XVIIIe siècle n'avait pu être remarqué jusqu'à présent.

Malgré l'opinion traditionnellement répandue, les enduits colorés à une seule couche se sont conservés tout au long du XVIIIe siècle. On les rencontre même, mais à titre d'exception, à la limite du XVIIIe et du XIXe siècle.

Il restait aux chercheurs à trouver des critères permettant de dater les enduits à une seule couche. La clef du problème a été donnée par le cinabre. Dans les enduits plus récents, la teneur en cinabre est soit sensiblement plus faible, soit égale à zéro. La couleur même des enduits a quelque peu évolué; d'abord brun rouge, on peut dire qu'ensuite ils sont brun jaune.

La différence entre les enduits à deux couches du début et du milieu du siècle et ceux de la deuxième moitié du XVIIIe siècle est tellement évidente qu'elle ne requiert pas d'analyse spéciale.

Passons maintenant à la couche colorée.

Des examens récents ont confirmé la justesse de l'idée que l'on avait de la structure de cette couche colorée: une couche sous-jacente colorée, le dessin des contours et la couche finale avec les glacis. Il y a, certes, une exception pour un tableau peint à la prima en 1725. Cependant, on peut dire que, au XVIIIe siècle, la technique picturale à plusieurs couches demeure immuable. Ce qui va changer au cours du siècle, ce sont les rapports entre ces différentes couches. Ceci est particulièrement sensible dans le portrait et surtout dans la façon de rendre le volume du visage. Au début du siècle, la deuxième et la troisième couches picturales conservaient les rapports de couleurs donnés par la couche sous-jacente. Les glacis ne faisaient qu'adoucir le contraste des ombres et des lumières. On peut dire que le volume était rendu par la couleur. Tout autre apparaît la peinture de la fin du XVIIIe siècle. La deuxième couche et la couche de surface nivellent les rapports colorés établis par la couche sous-jacente. La sensation de volume est alors surtout donnée par les glacis. Le clair-obscur joue ici le premier rôle.

Au cours de l'examen de la couche colorée nous avons prêté une grande attention à la composition des pâtes picturales, c'est-à-dire aux mélanges de couleurs

qu'utilisent les artistes. Sans nous arrêter maintenant aux mélanges spécifiques utilisés par les différents peintres, nous allons noter leurs points communs. Ils touchent surtout à la façon dont sont broyés les pigments. Pour les parties lumineuses du visage on utilisait des pigments broyés extrêmement fin. Agrandis 50 fois, ils apparaissaient comme des grains de poussière. Un semblable broyage est généralement associé aux colorants industriels du XIXe siècle. Maintenant nous savons qu'un phénomène semblable apparaît dès le début du XVIIIe siècle. Pour les parties sombres du visage, le pigment était broyé sensiblement plus gros. Peu à peu, le degré de broyage des pigments s'unifie pour devenir moyen. Dans les oeuvres artistiques du milieu et de la deuxième moitié du XVIIIe siècle on remarque que les particules sont plus grosses dans les lumières et plus fines dans les ombres. C'est un critère de plus pour dater les oeuvres.

Nous voudrions enfin dire quelques mots des pinceaux.

Nous savons, aussi bien par les recherches contemporaines que par les sources littéraires du XVIIIe siècle, que, pour travailler en détail les formes et les couches finales, les peintres utilisaient des pinceaux souples, de poils de blaireau, de putois ou d'écureuil. Les poils durs étaient utilisés durant les premières étapes du travail. Cependant, nous avons dé-

couvert que les pinceaux durs étaient utilisés pour les couches de surface aussi bien au début qu'à la fin du XVIIIe siècle. De plus, l'examen de la facture de la couche picturale permet d'affirmer que les artistes utilisaient des pinceaux plats déjà dans le premier quart du XVIIIe siècle. Il est difficile d'apprécier ce fait à sa juste valeur surtout si on se rappelle les affirmations de D.I.Kiplik selon lesquelles les pinceaux plats n'étaient apparus qu'en I800. Si les pinceaux plats n'étaient pas largement répandus au XVIIIe siècle, ils existaient cependant. Dans lescouches finales, les pinceaux durs étaient utilisés de différentes manières. Parfois, le pinceau dur servait seulement à souligner la forme, que le portrait ait été peint d'une façon libre ou avec une précision de miniaturiste. Dans d'autre cas, c'est toute la peinture de surface qui est appliquée à l'aide du pinceau dur redessine, pour ainsi dire, les contours de la forme.

A l'heure actuelle, nous n'avons pas encore réussi à mettre en évidence les différences de facture dans la surface de peinture, résultant de l'emploi de pinceaux durs aux diverses périodes du XVIIIe siècle. Nous espérons que, dans l'avenir, nous réussirons à résoudre ce problème.

Faisons maintenant le bilan.

Nos recherches ont permis d'apporter les précisions et modifications suivantes aux conceptions que nous avions jusqu'alors sur la technique picturale du XVIIIe siècle:

I. Utilisation d'enduits à deux couches dans le premier tiers du XVIII siècle.

2. Utilisation d'enduits à une couche dans la deuxième moitié du XVIIIe siècle.

3. Mise en évidence de l'utilisation du cinabre dans la composition de l'enduit.

4. Dégagement d'un critère permettant de dater les enduits.

5. Mise en évidence de la différence de nature du broyage des pigments composant les pâtes picturales, au début et à la fin du XVIIIe siècle.

6. Mise en évidence de l'utilisation de pinceaux plats dans le premier quart du XVIII siècle.

7. Mise en évidence de l'utilisation de pinceaux durs dans les couches finales.

Ces résultats sont capitaux pour l'expertise des oeuvres picturales du XVIIIe siècle.

78/20/5

RESTORATION AND ATTRIBUTION OF PORTRAITS BY YAKOV STRESHNEV

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ICOM Committee for Conservation
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RESTORATION AND ATTRIBUTION OF PORTRAITS BY YAKOV STRESHNEV

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The activity of Russian Art Restoration Centre includes the restoration of works of art and scientific-research work with the use of chemical, physical, radiografical, archives and history of art methods. We photograph and record all stages of the restoration. These investigations are used for the practice restoration and for history of art atribution. As a result of such methods we could determine the authors of nameless pictures and reconstruct the missing names of artists.

So in 1970 'The Portrait of A.P.Bakunin' by Streshnev was received for the restoration from the reserve of the Pushkin museum of art. The portrait, straight away, attracted general attention because of unknown name of artist, the old inscription on the back of the canvas '1832 Jakov Streshnev' and attractiveness of object. A.P.Bakunin was a Lyceum friend of Pushkin. The poet dedicated many of his poems to Bakunin's sister.

The radiograph and preliminary investigation of the portrait exposed some changes of drawing on the author's paint film and many parts of the latest paint films. At restorer's disposal there were only the results of chemical analisis and radiograph.

The search of auxiliary facts brought us to the

← article of V.Dudareva 'Istomino' in the magazine 'The Capital and Countryseat' No 68, 1916. Dudareva discribed the countryseat of descendents of the President of St.Petersburg Academy of Art A.N.Olenin. The collection of antiques and works of art included the portraits of the Bakunin's and their children, painted by serf artist Jakov Streshnev. There were little photographs of four portraits too. More than half a century passed from the moment the article was published, but the name of Streshnev was not mentioned in the literature. And his work never appeared at any expositions. So our first meeting with this artist has taken place at the Restoration Centre. The restoration was done by O.P.Pasternac under the guidance of Marennikova.

The paint film covered with cracks have darkened and become dirty to such an extend that the background became invisible. In the process of restoration the portrait was mounted on the new canvas, the inspiration from the anther's canvas was transferred to the back of the canvas, the cracks were strengthened and all deformations of the paint film and the canvas were levelled.

In the process of investigation it was discovered that the portrait in the whole was painted by the glue colour, easily washed off with water tampon. Under opaque painting there was dark coloured restoration varnish, which was at the face of Bakunin too. These two layers covered the painting of Streshnev. Test clearings if the little parts

have showed distortions and losses with brown priming underneath. The portrait had the traces of repeated restorations. It seems that the distortions have provoked an extensive and rough upper painting. Radiography revealed numerous losses of the paint layer; it revealed also the author's drawing.

It was necessary to clear the Streshnev's painting from the latest layers. The problem of removing the upper painting is one of the most difficul ones and requires and individual approach to every piece of art.

In this case there following factors in favour of the clearing: 1) qualitative difference between the lower oil layer and the upper glue one; 2) the ground with clouds hidden under the upper painting which was specific for the school of that time; 3) more natural and smooth drawing of the lower layer.

The photographs didn't allow to judge neither on the artists's manner nor the colour. An old reproduction of portrait differed from the original in details of drawing; it differed also from the radiography which revealed the author's drawing. It seems that the portrait was photographed between two restorations.

The work of clearing of the author's painting began with the removing of dirt, of upper painting and coloured restoration varnish; after that the original drawing had appeared, that could be seen on the radiograph: more free representation of the hair with curls, the right hand was

pressed to the body whereas at the upper painting the right hand was slightly put aside.

The paint layer on all the ground and on the frock-coat was distored greatly. The paint film was missing as far as to the priming in numerous part and in remaining ones it was scratched or washed off, as a result of which the upper films of fine multi-layer painting are absent.

One can suggest by the brush strokes remaining on the ground that the artist painted the sky with clouds. Such ground is typical for the romantic portrait style of that time.

In 1973 after the work was finished three portraits by Streshnev from the private collection of the writer N.M.Davidova were received for restoration by the Restoration Centre. These were representations of Bakunin's children: two double portraits - a boy and a girl which were reproduced in 1916, the third portrait - half-length portrait of the same firl.

'Portrait of Olya', canvas, oil, 53.5 x 43.5

'Portrait of Tanya', canvas, oil, 53.5 x 43.5

'Portrait of Tanya', half-length, 35.5 x 29.7 canvas, oil.

There is reference to the last portrait in Dudareva's article, and there is no inscription on the back side of the portrait. However, there is no doubt about the authorship of this painting because of the same manner and technique of the painted face known to us by the portrait of

Tanya Bakunina reproduced in the magazine.

The restoration of the portraits done by V.M.Tanaev is similar to the restoration of "Bakunin's portrait": mounting and removing the latest layers, after which the author's drawing appeared in the numerous parts and the colouring of the portrait changed. This change can be clearly seen on the photographes of the portrait of the boy: on the photo before the restoration the base of the table is round, on the photo after the restoration the base of the table is criss-cross.

So four works by the forgotten serf artist Jakov Streshnev have been restored at the Restoration Centre. In 1974 'Bakunin's portrait' was exposed for the first time at the V11-th Restoration Exhibition in Moscow and Leningrad. Due to it the name of Streshnev became known to the art amateurs. In 1975 the fifth portrait of this artist was exposed for the first time at the exhibition 'Unknown and Forgotten Portraits' in the Tretjakov gallery. It was the 'Portrait of A.B.Bakunina' - the first wife of A.P.Bakunin (c.,o. 61x46). There was inscription on the back side: 'Anna Borisovna Bakunina. Born in 1802, 15 November. Died in 1835, February, 11. Buried in Moscow, Novodevichy Monastery'.

The condition of the portrait was worse than that of the other ones. The restorer from the State Museum of the Fine Arts - Zinovjeva - restored this portrait. After the restoration and exhibition both works by Streshnev were

returned to the reserve of the Pushkin Museum of Arts, and the children's portraits - to Davidova's collection.

All these portraits were painted on the monolayer brown grounds, the painting is scumbled multi-layer with glazes. The colour of the portrait is composed mainly of green, brown and black shades. Streshnev skillfully used white colour enlivening somewhat dull shade of his paintings. He painted the sky with clouds as a ground on all the portraits. It is the reason of spatial depth and romantic spell of the portraits in the whole. The portraits were painted with assurred modelled faces and with characteristic washing off of the ends of eye-brows. The works by Streshnev followed the good artistic school. May be it was the school and the lessons of A.N.Olenin (1763-1843) - archeologist, historian and artist, president of St.Petersburg Academy of Arts. Besides, the artists who were often coming to Istomino, might influence the gifted serf artist.

Thus the works by Jakov Streshnev which have written a new page into the history of Russian art, have been restored and brought to one place.

78/20/6

PRINCIPLES OF EXAMINATION OF THE WORKS OF ART ATTRIBUTED TO I.K. AIVAZOVSKY

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As Aivazovsky himself witnessed the number of his works was about six thousand. The popularity of his works was so great that even in his life-time there was a lot of imitations, replicas and falsifications that was circulating in the antiquarian market. One of such masters-imitators was mentioned in a magazine "Russkaja starina", 1878. His pictures were touched by the hand of Aivazovsky himself and were of great demand among unexacting admirers of the great painter of sea-scapes. Wonderful imitations were made by Solntsev - a teacher of icon-painting in the Petersburg Academy of Arts. Besides, the author himself repeated his works and made a great number of variants of the same composition.

Even now Aivazovsky remains one of the most popular artists of the antiquarian market. Practically every museum of the USSR has in its collection works of this artist, but many of his works are still in private collections. So at arrival to a museum of a picture attributed to Aivazovsky it is necessary to identify false and imitative works. It is required a thorough technological analysis because stylistic examination cannot lead to certain conclusions.

Every work to be analysed undergoes first of all exami-

nations aimed to ascertain the period of time of its creation. Further examination is based on the comparison of the dates of analysed work and the dates received during the examination of a great number of authentic works of the painter.

The analysis of works of the Picture Gallery of the city of Feodosia has demonstrated that the painting technique of the artist differs greatly of the academic manner, which presumes a preliminary study of nature, a detailed drawing and a developed preliminary painting. Even in the early works of Aivazovsky made in the Petersburg Academy of Arts there is a significant difference in the technique in comparison with the works of other painters.

For Aivazovsky the preliminary study of nature consisted in the very schematic drawing outlining the basic points of the composition. Then this schematic drawing is being transferred to a primed canvas. A preliminary painting in a traditional sense of the word is absent. Instead of it the canvas is painted by three main colours which will further serve not only as a preliminary painting but also as a basic paint layer.

A clear interdependence can be found between the character of the painted surface and the linen and ground used in canvases of Aivazovsky. During the whole period of his creative work Aivazovsky used fine-grained and medium-grained linens of direct weaving. Fine-grained and

medium-grained linens of direct weaving with the threads of equal thickness of warp and seft are typical of his works with smooth enamelled like surface in the late 30's and early 50's. Double coated grounds (the upper coat containing whiting and the lower one - ochre mixed with whiting) with oil binder are characteristic of these linens. Double coated grounds together with the fine grain of the linen and fairly great thickness of the ground make up the smooth surface. Double coated grounds with oil binder can occasionally be found in all the artist's works. It has not yet been cleared up if it was the artist's technique or it was a mere use of the specially prepared factory-made grounds. Single coated oil grounds and the linens of direct weaving with the threads of unequal thickness of warp and weft are characteristic of his painting in the 70's and 80's. In the 80's in a number of his works a linen of diagonal weaving was used for the first time. In the late 70's the grain of the linen was becoming larger and the relative thickness of the ground was decreasing. As a result the painted surface became more dead and lost its enamel shine.

In the 80's and 90's Aivazovsky widely used emulsioned grounds on the medium-grained linens which allowed him to make the painted surface even more dead. Each type of the painted surface corresponds to certain chronological period of the painter's creative activity. But in each period one can come across several works with the type of the painted

surface of the previous one, which indicates that the painter intentionally selected the type of the linen and ground.

According to many evidences of his contemporaries Aivazovsky painted his works during one session. The investigation of the texture of the painted surface of his canvases showed that it was not true. Among his works one can find many canvases whose parts were painted on the dry coat of paint. It only means that they were made at least during two seances.

Since the ground of Aivazovsky's painting is of great radiographical density and pastes of paint contain roughly the same portion of the white lead (it makes the X-ray photographs not so much contrasting) the radiographical investigation does not allow to establish clearly the principles of the construction of painted coat. The most suitable technique of determining the character of the construction of painting is a method of making photographs of fragments in slanting beams. That technique allows to establish a character of the painter's touch. The investigation of the painter's manner by the means of macrophotographs of texture of the painted surface is the last and major stage of the examination of the works attributed to Aivazovsky. This technique made it possible to establish features specific of the artist's manner.

Aivazovsky used technological cliches which he applied at the early stage of his creative activity and which had

undergone insignificant changes since that time. The principle of the form construction remains unchanged throughout his life. After coating of the linen with major colours on damp paint coat the main elements of composition are being worked out: waves, mountains, shores, etc. Aivazovsky's palette consists of a few number of colours. It should be noted that the forms of the objects on pictures plane are created by the means of texture rather than by the means of colours. Large planes are coated with liquied pastes by the means of b bristly brushes. And at this stage he used "Z"shaped touch. At the next stages Aivazovsky put a layer of more liquid paste on the texture of these touches so that not to cover it. Three types of brush movement can be found in the major painted coat: so called "swallow tail", "loops", "herring-bone".

The zigzag touch is very characteristic of Aivazovsky. He used it both for coating large background planes and for the painting of certain details. The same texture method was applied for painting of various details: sea waves in his canvases "The Island of Crete", 1867, "The Shipwreck", 1876; and ears in "The Harvest Time in the Ukraine" were painted absolutely in the same manner. And the same can be said about the moorage stones in "On the Island of Rhodes" and about the board of the boat in "Walking on Waters". The published photograph allows to judge on the features of his zigzag stroke. The direction

of the touch movements makes it possible to assume that Aivazovsky painted by right and left hand.

The fragments comparison of pictures painted with intervals of ten years and more testifies to the fact that they have identical texture construction. The changes took place mainly at the expense of the decreasing of paint paste density on those parts of canvases where details were depicted. Applying technique of painting of composition details on dry coat of paint in the 40's and the 60's Aivazovsky achieved a great paint relief (impasto). But from the 70's this relief began smoothing down and came to naught by the 90's.

The investigations of the canvases allow anable us to make the following conclusions which considerably change the traditional view on Aivazovsky techniques.

1. Each type of the surface of paint and the type of the ground and linen corresponds to certain period of Aivazovsky's creative activity.

2. Evolution of the character of the painted surface develops from the smooth enamellyed-like surface overloaded with paint paste to the dead surface with clearly seen grainly texture of the linen and thin paint layer.

3. The artist works out his techniques at the early period and widely applies them during the whole period of his creative activity.

4. Aivazovsky painted his canvases during several sessions.

The results of the technical investigation of Aivazovsky's canvases are constantly applied during examination and identification of the works attributed to this artist. The coincidence of data on works to be examined with the results of the investigation is the main criterion for the distinguishing of original Aivazovsky's paintings from fakes and copies.

78/20/7

IDENTIFICATION OF PIGMENTS IN PAINTINGS WITH X-RAY POWDER DIFFRACTION METHOD - POSSIBILITIES AND LIMITS

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Stephan Fitz

In painting examination the Debye-Scherrer x-ray powder diffraction method is commonly used for the identification of pigments. In spite of the common application only little attention has been paid to optimum experimental conditions. Better knowledge of the possibilities and limits involved in this method may lead to optimal results.

Fixing of the sample

The sample to be examined is usually fixed on a thin rod or in a capillary[1) 2)]. In pigment identification the samples are extremely small in most cases. Their fixing may involve some difficulties. Mounting the sample at the end of a glass filament with shellac, glue, some other adhesive or with silicon fat may cause fogging of the films, if too much of the adhesive has been used. In addition, the glass filament itself may produce a background blackening due to diffuse x-ray scattering. Some mitigation of this undesirable effect may be achieved using the lower absorbing Lindemann glass. Instead of glass, the rods the samples are fixed on may be made of organic, x-ray amorphous material, e. g. collodium[1) 2)].

Fixing the sample on a thin rod involves some disadvantages. The use of an adhesive not only contributes to a higher background on the films, but removing the sample after exposure to x-rays for further analytical examinations by other methods is only possible after manipulations with solvents. Furthermore, storing a mounted sample over a longer period presents problems, because it might get lost or be contaminated with dust. These problems do not come up when the sample is poured into a commercially available capillary made of Lindemann glass, where it can be sealed easily. Pouring small amounts is not an easy procedure to handle. But with some practical experience a technical assistant will soon be able to pour microamounts into capillaries. With the aid of an extremly thin glass filament we can pour samples of 0,02 mm cross section into capillaries with a diameter of 0,1 mm.

Background blackening of the films

In some cases the exposed films will be badly fogged. Besides incorrect or excessively long storing of the x-ray film material, the cause of fogging can have various reasons.

The primary monochromatic x-ray beam can initiate fluorescence radiation of the sample. Cu-K_α radiations, usually used in routine investigations, produces for example, extremely strong fluorescence of iron molecules. Iron containing samples cause homogenous blackening of the film. Once recognized, a change of the x-ray radiation provides much better results. In the case of iron-containing samples, Fe-K_α, Co-K_α or Cr-K_α radiation shall be used.

A content of amorphous material in the sample (e. g. mediums) or surrounding material (e. g. adhesive, glass) leads to more or less intensive background of the films due to the scattering of the x-rays on that material. This usually only occurs in some areas of the diffraction pattern. Reducing the content of these materials by the use of glass capillaries instead of rods and by a more effective sampling provides better results. Air molecules also contribute to film blackening, observable especially in the case of long exposure times. This effect can be mitigated by using a vacuum during exposure time.

The width of the lines in an x-ray diffraction pattern

In order to obtain a diffraction pattern, which allows simple and exact evaluation, attention should be paid, not only to the ratio of the intensities of lines but to the background. Efforts should be made to receive clear and sharp lines.

The width of the lines in a diffraction pattern depends on the convergence of the primary beam and the cross-section of the sample. Since in general commercially available cameras are used there is no possibility of exerting any influence on the beam's convergence. It is sufficient.

A smaller cross-section of the sample leads to sharper lines. This statement is valid only to some extent. If the crystallites of the pigments (not the total sample size!) are smaller than 0, 5 µm, the interferences become broader and weaker. On the other hand, crystallites larger than 20 µm lead to grained interferences. Usually the crystallites in pigment grains are in the right proportions.

As the total cross-section of the sample influences the width of the lines obtained, it should be kept small. In respect to the primary beam, a badly adjusted rotating sample has a cross-section which is identical with the diameter of the circle the sample is rotating on. In general, the size of the sample should never exceed the cross-section of the primary beam - it should be "bathed" in the x-rays.

Optimum sample size

With increasing thickness of the sample the amount of radiation transmitted through the crystals is reduced due to absorption. At the same time the total amount of radiation deviated by diffraction increases with sample thickness. Knowing the composition of the sample the optimum sample size can be estimated[2]. The evaluated optimum sample sizes of some pigments for Cu-K_α radiation are shown in Table 1. If the monochromatic radiation is changed, the optimum sample sizes may vary strongly as a consequence of completely different absorption conditions.

Table 1
Optimum sample size [μm] (Cu-K_α radiation)

Compound	Optimum sample size
White lead $2PbCO_3 \cdot Pb(OH)_2$	0,02
Gypsum $CaSO_4 \cdot 2H_2O$	0,14
Silica (Quarz) SiO_2	0,22
Titanium dioxide (Rutile) TiO_2	0,04
Chalk $CaCO_3$	0,10
Zinc white ZnO	0,07
Baryte $BaSO_4$	0,02
Cinnabar HgS	0,01

Azurite $2CuCO_3 \cdot Cu(OH)_2$	0, 08
Iron oxide red (Hematite) Fe_2O_3	0, 02

Only in a few cases, in the practice of pigment identification, a size of the sample which corresponds to the theoretical value can be reached. The best diffraction patterns should be achieved with samples of approtimately $0,1 \pm 0,05$ mm cross-section. Nevertheless, samples should rather be chosen smaller, because sampling is a destructive method.

Detection limits of pigments in mixtures

Applying the x-ray diffraction powder method to the identification of pigments in a painting, the investigator should know where the detection limits of compounds contained in a mixture are. Samples of paint usually contain two or more pigments in a mixture, single compounds occur comparatively rarely.

In most cases the x-ray absorption of the individual components in a mixture is not equal. The intensities observed are not proportional to the concentrations. A mathematical treatment of the intensity ratio in mixtures is possible[3)], but some assumptions have to be made, which do not correspond to reality.

In a series of artificially prepared mixtures the detection limits can experimentaly be evaluated. As an example, the detection limits of some pigments mixed with white lead (one of the most frequently occuring pigments in painting) have been evaluated. The results are given in Table 2.

Table 2
Detection limits of some pigments in a binary mixture with white lead

Pigment	Detection limit (weight percent)
cinnabar	5
zinc white	15
baryte	15
ultramarine (synth.)	20

The results show that even a relatively high content of pigments

with low absorbing power is not detectable when present in a mixture with highly absorbing compounds, as for example with white lead.

The x-ray powder diffraction method gives no evidence of low absorbing pigments (even in quantities which cannot be neglected as traces) if strongly absorbing pigments are present. In order to raise the detection limits, it may be helpful to separate the ground from the paint or to try isolate the grains of different pigments under a microscope.

Interpretation of x-ray powder diffraction patterns

To interpret a diffraction pattern, the film can be directly compared with standard films prepared from pigments of a known composition. A complete collection of these standard films, recorded with the same radiation and camera radius, should be available to the investigator. Since this is not always possible, the diffraction pattern has to be evaluated in respect to the d-values and the relative intensities of the observed lines. The pigments can be identified with the aid of the ASTM card-index. The searching method is described elsewhere[4].

Some difficulties may arise when the ASTM-card-index is used. The given data is evaluated with various x-ray diffraction techniques or various radiations. A direct comparison of experimental data with the values given in the index is not always possible.

In addition, not all the pigments are listed in the index. Because of the limited number of pigments, it seems useful to have a special index of powder diffraction data of all pigments used in painting. König's book provides some useful information[5], but the reproduced films of various diffraction patterns of pigments are still incomplete and not suitable for direct comparison with actually recorded films. At the "Forschungsinstitut des Deutschen Museums" a complete catalogue of pigments is being prepared. The d-values are given together with relative intensities for Cu-K_α and Fe-K_α radiations. In addition, all lines observed are given in a simple graphical scheme which allows comparison with the standard d-values after graphical transscription of the experimental data.

Evaluation of relative intensities

Evaluating the d-values of a diffraction pattern presents no problems. More difficulties are connected with the evaluation of the relative intensities.

The measurement of intensities with a microphotometer is very time-consuming and is not necessary if a qualitative analysis is carried out. The visual estimation of intensities, (which is sufficiently accurate) after some training is much easier. The estimated intensities should be classified into five groups: very strong (vs), strong (s), medium (m), weak (w) and very weak (vw). Very strong lines correspond to a relative intensity of 100, strong lines to 60, medium lines to 25, weak lines to 10 and very weak lines to 5 or less. It is easily possible to make an additional more detailed classification.

The x-ray powder diffraction method has some disadvantages, e.g. the low sensity in the case of mixtures. On the other hand the extremely small sample amounts necessary for examinations (the samples not being destroyed), and the relatively simple technique makes the method a useful tool in the hands of the scientist especially when used in addition to other analytical methods.

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78/20/8

CONTRIBUTION A L'ANALYSE DES LIANTS MIXTES

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CONTRIBUTION A L'ANALYSE DES LIANTS MIXTES

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La méthode des tests spécifiques utilisée au Laboratoire de Recherche des Musées de France permet dans un certain nombre de cas d'identifier sur coupes minces un mélange de liants à l'intérieur d'une même couche picturale.

On parvient à distinguer entre eux les liants tels que oeuf, huile et colle, oeuf et huile qui sont tous constitués de lipides et de protéines. On utilise pour cela simultanément les résultats obtenus par le test de chauffage et ceux obtenus par les colorations spécifiques au Noir Amide.

Divers exemples sont cités pour illustrer la méthode.

Nous avons déjà publié (1) (2) la méthodologie mise au point au Laboratoire de Recherche des Musées de France pour la mise en évidence in situ sur coupes minces des constituants principaux (lipides et protéines) des liants de peinture. Cette méthode opère par comparaison avec des étalons de référence et est susceptible de rendre de grands services dans les Laboratoires de Musées car elle permet dans un certain nombre de cas de localiser à l'intérieur d'une même couche picturale des mélanges de liants.

On rapellera que le principe est basé sur l'observation des différences avant et après chauffage pour l'examen des corps gras, et des colorations spécifiques pour les protéines.

Dans le cas des lipides il y a formation de gouttelettes brillantes et suivant leur nature et la quantité présente, brunissement plus ou moins intense de la couche. L'ordre de grandeur de la température utilisée varie de 170° à 250°. Il faut signaler que lorsque le pigment est une terre ou du vermillon l'huile est mal mise en évidence par ce procédé. Pour des analyses semi-quantitatives il est préférable de comparer les effets du chauffage sur des couches contenant un même pigment comme le blanc de plomb.

Pour les protéines, on utilise des réactifs contenant un colorant, le Noir Bleu Naphtol 10B à différents pH, ce qui permet de reconnaitre les protéines suivant leur teneur relative en acides aminés basiques. Trois réactifs type ont été utilisés selon les compositions suivantes :

- NA_1 (Noir Amide $_1$) : 1 g de colorant dissout dans 450 cm^3 d'acide acétique glacial, 450 cm^3 d'acétate de sodium 0,1N, 100 cm^3 de glycérine. Tous les groupements amines sont ionisés et le colorant se fixe de façon satisfaisante sur les protéines comme le jaune d'oeuf.
- NA_2 : 1 g de colorant dissout dans 450 cm^3 d'acide acétique (N), 450 cm3 d'acétate de sodium 0,1N, 30 cm^3 de phosphate disodique 0,2N, 70 cm^3 de glycérine. La présence de phosphate est nécessaire pour "démasquer" les protéines incluses dans une pellicule huileuse séchée.
- NA_3 : 1 g de colorant dissout dans 900 cm^3 d'eau et 100 cm^3 de glycérine. Avec ce réactif neutre, seules les protéines très chargées en groupement amines (comme la gélatine) sont colorées.

Dans chaque cas, les échantillons après coloration pendant une minute environ sont rincés dans l'eau acétique.

La méthode est appliquée à l'étude de mélanges lipides-protéines contenus dans une même couche picturale ; dans ce cas, le test du chauffage et au moins un des tests protéiniques sont positifs. Il s'agit d'interpréter les résultats des tests pour distinguer entre eux les différents liants qui contiennent des corps gras et des protéines selon les conclusions du travail préliminaire déjà publié (2) sur les liants constitués de mélanges d'oeuf, d'huile et de colle. Le liant ainsi défini peut être, soit un mélange d'huile et de protéine (colle ou albumine), soit un mélange à base d'oeuf (jaune seul ou entier ou oeuf mêlé d'huile).

<u>Emulsion d'huile dans la colle</u>

C'est un liant mat, sensible à l'eau, en général riche en col-

le, qui se rencontre principalement sur les polychromies.

Le tableau ci-dessous résume les renseignements obtenus lors des différents tests effectués sur un échantillon du XIXème siècle comprenant trois couches.

tests	couleur	chauffage 225°	NA_3	NA_1	conclusion
1ère couche	jaune	-	++	+	colle
2ème couche	blanche	++	++	+	huile + colle
3ème couche	jaune	+++	-	-	huile

Pour la couche 2 l'intensité de coloration avec le NA_3 est nettement supérieure à celle obtenue avec le NA_1 ce qui exclut un mélange à base d'oeuf. La couche blanche est donc constituée d'un liant contenant à la fois de l'huile et de la colle.

Emulsion de protéine dans l'huile

C'est un liant essentiellement huileux que de nombreux peintres ont utilisé dans leurs couleurs claires probablement afin d'éviter le jaunissement de l'huile.

Le test du chauffage est nettement positif, mais ne révèle pas l'hétérogénéité du liant.

Le réactif NA_2 permet une localisation très précise de la phase protéinique même incluse dans une huile séchée. On peut observer après coloration, les grains protéiniques bien individualisés, fortement colorés, de taille relativement homogène comprise entre 1 et 10 microns. Le faciès de l'émulsion est plus précis sur écailles que sur coupes. Les réactifs NA_1 et NA_3 ne donnent pas des colorations suffisantes pour que l'on puisse en déduire la nature de la protéine émulsionnée. L'étude de ce liant est traité de façon plus complète dans une précédente publication (2).

Jaune d'oeuf

Dans ce cas le test du chauffage est caractérisé par un brunissement homogène variant du beige au brun lorsque la température varie de 200° à 225°. L'intensité de coloration avec le réactif NA_1 est généralement supérieure à celle obtenue avec le réactif NA_2. C'est particulièrement vrai pour les couches contenant de la laque rouge que le réactif NA_2 ne colore que rarement. Nous constatons là encore une certaine influence des pigments qui reste assez difficile à expliquer.

Oeuf entier

Le plus souvent, en présence d'oeuf entier, l'intensité de coloration avec le NA_2 est supérieure à celle avec le NA_1.

Après chauffage à 250° d'une écaille-échantillon, on observe nettement trois zônes distinctes, l'une brune révélatrice du jaune d'oeuf (comme ci-dessus), la seconde beige mettant en évidence jaune et blanc d'oeuf et la troisième restant blanche et ne contenant que de

l'albumine. Si donc sur une coupe après chauffage, une hétérogénéité marquée est visible, on peut dire que le liant est de l'oeuf entier. Toutefois si le chauffage tout en étant homogène est très nettement faible par rapport à la quantité de protéine révélée par les réactifs, on peut aussi conclure à la présence d'oeuf entier.

Le tableau ci-dessous résume les résultats obtenus sur les essais effectués sur 70 échantillons de peinture de Primitifs Italiens.

nombre d'essais	NA_1	NA_2	chauffage 225°	conclusion
33	++	+	++	jaune d'oeuf
8	++	++	++	jaune d'oeuf
10	+	++	++	oeuf
6	++	+	+	oeuf ou oeuf entier si chauffage hétérogène
9	+	++	+	oeuf entier
4	++	++	+	oeuf entier

Lorsque nous concluons à la présence d'oeuf c'est que nous ne pouvons pas préciser s'il s'agit de jaune d'oeuf seul ou d'oeuf entier.

Notre étude repose sur un trop petit nombre d'échantillons pour que l'on puisse en tirer des conclusions générales ; certaines tendances commencent cependant à se dessiner : ainsi l'étude de trois tableaux de Giotto a montré que ce peintre utilisait de l'oeuf entier pour les jaunes et du jaune d'oeuf pour les chairs.

Huile et oeuf

Ce cas est illustré par des échantillons prélevés sur un tableau de Rembrandt. Le caractère très gras du liant apparait dès 200°. Le réactif NA_1 révèle la présence modérée de protéines que les réactifs NA_2 et NA_3 ne mettent pas en évidence. La quantité de jaune d'oeuf ainsi révélée étant trop faible pour justifier l'aspect après chauffage, nous concluons donc à la présence d'un liant mixte composé d'oeuf et d'huile.

Il existe malheureusement un certain nombre de cas douteux. En effet le réactif NA_1 qui seul permet la localisation de l'oeuf dans l'huile contient de l'acide acétique glacial qui dissout un certain nombre de substances résineuses ce qui conduit parfois à donner un aspect opalescent légèrement bleuté qu'il ne faut pas confondre avec une coloration (le matériau de la couche picturale devient dans ce cas pâteux et se ramollit).

Conclusion

Il apparait donc que la méthode des tests spécifiques est particulièrement bien adaptée à la mise en évidence des émulsions de protéine dans l'huile. Il est également possible d'affirmer qu'un liant contient de l'oeuf, mais il est encore parfois difficile de préciser s'il s'agit de jaune d'oeuf seul, d'oeuf entier ou d'un mélange oeuf-huile.

Nous citerons pour terminer un exemple tiré de Niccolo del Abbate qui montre les possibilités de la méthode qui a permis de localiser dans chaque couche quatre liants différents : de la colle, de l'huile, une émulsion de protéine dans l'huile et de l'oeuf. Aucune étude globale n'aurait permis d'analyser aussi finement un échantillon tel que celui-ci. Il en résulte que malgré quelques cas difficiles ou ambigus que l'expérience devrait permettre de résoudre la méthode des tests spécifiques apporte à la connaissance des liants de peinture ancienne une contribution importante.

(1) MARTIN E., Some improvements in techniques of analysis of paint media, Studies in Conservation, 22 (1977) 63-67

(2) MARTIN E., Etude des liants de peinture. Application des tests sur coupes minces à l'identification des émulsions, Annales du Laboratoire de Recherche des Musées de France, 1977.

78/20/9

TECHNOLOGICAL INVESTIGATION OF THREE ENCAUSTIC ICONS FROM THE MUSEUM OF EASTERN AND WESTERN ART IN KIEV

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In 1973-1977 three encaustic icons: "The Martyrs" of 6th-7th century A.D., "Sergius and Bacchus" and "Our Lady with the Infant Christ", both of 6th century A.D., arrived from the Kiev Museum of Eastern and Western Art to the All-Union Central Scientific Research Laboratory for Conservation and Restoration of Museum Artistic Works (VCNILKR) for investigation and restoration. The icons were brought to Russia in the middle of the nineteenth century from the Monastery of St Catherine at Mount Sinai. The paintings did not essentially change only missing fragments were renovated and varnish was applied to the icons with the result that the restoration painting partly overlapping the authentic painting. "Our Lady with the Infant Christ" was the only icon whose original size was altered. Its three sides were sawn off and the upper corners were lopped off also. A missing panel part on the right side of "The Martyrs" had been restored previously. The size of "Sergius and Bacchus" did not change but its original superposed frame, however, had been lost. The frame of "The Martyrs" is made of the same tree as the panel which has a profile for a down wad sliding shield and is painted with wax paints with no ground; the shield itself is lost. Both "Our Lady with the Infant Christ" and "Sergius and Bacchus" have original panel edges with no ground or paint layer on them.

Each icon was painted on one panel. The tree species have been determined as stone pine in the case of

"Sergius and Bacchus", linden in the case of "The Martyrs" and cypress in the case of "Our Lady with the Infant Christ".

The front surface of "The Martyrs" has incisions which were made for better linking of the ground to the panel. All the panels were applied to grounded in an identical manner, the thickness of the ground proportionally reduces from the upper edge downwards.

There are different points of view on the original composition and size of the icon "Our Lady with the Infant Christ" in the literature. The observed nature of the distribution of the ground on this icon, however, makes it possible to come to the conclusion that its sides were sawed a little.

I. Physico-optical investigations

Photography of the icons in the light of visible luminescence induced by ultra-violet radiation as well as infrared photography revealed the places and the extent of intervening restoration efforts. Photography in reflected ultra-violet rays enabled to determine the nature and degree of surface layers.

The most interesting information was obtained while X-raying "The Martyrs". The radiogram served to establish non-uniformity of the ground thickness due to mechanical damage as well as the heterogeneity of the new fragments. The peculiarities of painter's style were revealed. Unlike the other two, this icon was painted with an undercoating serving at the same time as the drawing. In the underdrawing all the objects are outlined: clothes with folds and creases; crosses, heads (not only faces); inscriptions and the All-seeing Eye.

Contrary to traditional idea of the en/caustic

technique the icons were painted with a brush. Microscopic examination of the surface texture revealed distinct long brush strokes. Moreover a fragment of a bristle was found in the paint layer of "The Martyrs". The pattern of the bristle's cuticle is similar to that of hoofed animals' hair cuticle.

II. Investigations of materials
Inorganic materials

Methods of microscopic, microchemical, emission spectroscopic, micro- X-ray spectral and X-ray diffraction analyses were applied for the study of the icons' inorganic materials.

(a) "The Martyrs"

The cross sections for the study of the paint layer were prepared. The layer of one colour is 200-250μ thick transparent layers contain a comparatively small amount of pigment mixed with the binding medium. The less mechanical adhession between paint layers on this icon is explained by this fact. The grains of crystal pigments are rather big from 10 to 50μ. A thin layer of transparent wax ($\sim 50\mu$) covers the paint layer of the surface.

It was found that white lead /$2PbCO_3 \cdot Pb(OH)_2$/ had been used as the white pigment. A large amount of tin was detected in white lead by means of semi-quantative micro X-ray spectral analysis.

A large admixture of tin was also found in the orange pigment covering the frame had been X-ray diffraction showed that red lead Pb_3O_4 used as the orange pigment. Probably, white lead and red lead had been prepared from material that contained a large admixtu-

re of tin. A large amount of iron was detected by microchemical and emission spectral analyses in the samples of the yellow paint of the clothes of the Man, the clasp of the dress of the Woman as well as her hair. In small angles there were revealed very small diffuse reflections which could not be identified. After heating the particles of the yellow pigment grow reddish-brown in colour and the Debye-Scherrer pattern showed interference peaks corresponding to the following interplanes distance values: $d_1=2.70$; $d_2=2.50$; $d_3=1.82$; $d_4=1.66$. These values coincide to a sufficient degree of accuracy with the tabular data of hematite-iron oxide Fe_2O_3. It can be presupposed that ochre was used as the yellow pigment with iron hydroxide $Fe_2O_3 \cdot nH_2O$ (limonite) being the colour carrier; because of limonite has amorphous structure small diffuse reflections were observed in the Debye-Scherrer pattern. Ochre was mixed with bright yellow crystals-auripigment As_2S_3. The crimson coloration of the Martyrs' cloak fluoresced in the direct ultra-violet radiation giving orange tint; it is known that natural madder is characterized by that property. The pigment's Debye-Scherrer pattern revealed gypsum $CaSO_4 \cdot 2H_2O$. It is likely that in this case gypsum had been used as the base of the organic pigment. This pigment mixed with white lead had been used to redden cheeks and lips and it was also found in the paint of clothes of the woman, mixed with blue vitreous crystals of another pigment, possibly Alexandrine frit. A large amount of copper in the sample of the green paint taken from the Martyrs' clothes was revealed by microchemical and spectral analyses. X-ray diffraction failed to reveal the crystalline structure of this pigment. Fragments of an inscription made on a very dark, seemingly black,

background were preserved in the upper part of the icon. As it was shown the optic effect of the "black" background was caused by the green copper pigment lying upon the dark-blue crystals of ultramarine.

Microscopic investigation of the author's ground revealed a friable, porous mass consisting of transparent needle-shoped crystals. The analysis of this substance by X-ray diffraction showed that it consisted of anhydrous calcium sulphate - $CaSO_4$. X-ray diffraction of ground samples of restoration insertion fragments detected calcite $CaCO_3$ and white lead in the form of $2PbCO_3 \cdot Pb(OH)_2$. The obtained results indicate that repeated efforts were undertaken at different times to restore the icon.

(b) "<u>Sergius and Bacchus</u>"

It was shown by the microscopic investigation sections of the paint layers of this icon are non-transparent, much thinner than those of "The Martyrs" - varying from 50μ to 100μ and contain a large quantity of fine dispersion of crystalline pigments. The size of pigment grains varies from 1 to 20μ.

White lead $2PbCO_3 \cdot Pb(OH)_2$ was employed as the white pigment. The blue-green background of the icon owes its colouring to smalt. The dark-blue outline of the nimbus is painted with ultramarine. Both smalt and ultramarine are whitened with white lead. Cadmium was found in the red outline of the nimbus. X-ray diffraction analyses has detected that the red pigment is cadmium sulphide.

Sergius's clothes are painted with a heavily whitened mixture of a fine dispersion of ultramarine and a crimson pigment. The structure of the latter could not be revealed but in the ultra-violet radiation this pig-

ment fluoresced with an orange tinge just like in the case with "The Martyrs".

The icon's ground is of two layers, the lower one being thicker and consisting of calcite while the upper one is of greater density and it is thinner and consists of white lead.

(c) "Our Lady with the Infant Christ"

The ground has one layer, it is dense and consists of calcite. The blue background of the icon is painted with azurite, the size of crystals varying from 30 to 400 μ . The backround surface is rough and uneven, due to the presence of large crystal grains. A comparatively small amount of the green pigment grains were found among azurite crystals under microscope. X-ray diffraction revealed that those were grains of malachite $CuCO_3 \cdot Cu(OH)_2$.

It can be supposed that in this case malachite is an accidental admixture of poorly purified azurite. White lead $2PbCO_3 \cdot Pb(OH)_2$ was employed as white paint. Pb_3O_4 was found in the outline of the nimbus. The clothes of "Our Lady and the Infant"are painted with a subtly whitened mixture of soot and cinnabar. All the paint layers are non-transparent containing a large amount of pigment.

In those cases when it was not possible to remove the binding media completely while examining the pigment structure interference peaks of the crystalline pigment along with interference peaks with the following interplanar distance values: d_1=4.20; d_2=3.76; d_3=2.97; d_4=2.49; d_5=2.23 could be seen on the debayegram. A similar debayegram was produced when examining the layer of yellow wax overlaying the paint layer of "The Martyrs".

In our opinion, the above mentioned interplanar distance values are due to the presence of beeswax crystallized at room temperature.

II. Organic materials

The investigations were carried out by means of infrared spectroscopy. Small fragments of the paint layer were extracted with chloroform. The obtained solution was filtrated through a glass filter and applied by a capillary on the KBr plate. While examining the solid residue it was pressed with KBr into pellets. The infrared spectra were recorded with a "Perkin-Elmer 257" (4000-625 cm^{-1}).

Fig. 1 shows IR-spectra of the fragment extracts:

a - blue background of "Sergius and Bacchus"; b - the layer overlaying the golden nimbus of the saint ("The Martyrs"); c - the yellow part of the saint's clothes; d - the red paint of the clothes; e - the green part of the saint's clothes; f - the dark-blue background of "Our Lady with the Infant Christ".

There are the bands characteristic of beeswax in these spectra /1/. Some differences from the spectrum of pure wax (Fig. 1 g) were noted in the IR-spectra (a, d-e). In spectrum (a) there is an additional band at 1510 cm^{-1} with shoulder at 1540 cm^{-1} while in spectra (d, e) there appears a broad band at $\sim$1600 cm^{-1}.

The appearance in spectrum (a) of a band with shoulder in the 1500-1540 cm^{-1} region is evidently due to the presence of an admixture of fatty acid salts with metal cations (1), Punic wax in the extracted substance. It is more difficult to interprete the band at $\sim$1600 cm^{-1}. We supposed that some admixture to beeswax had been added. To verify this suggestion we prepared and examined mixtures of wax with resins-dammar, mastic,

sandarac and colophony. The IR-spectrum of the substance extracted after melting together wax and dammar in 2:1 ratio there appears a new band at $\sim 1600\ cm^{-1}$ which is absent in the spectra of pure wax and dammar. It was not seen either in the spectra of wax with other resins. In the case of spectrum (d) the appearance of this band may be due to varnish covering the given section of the icon. It is most likely that dammar (the varnish spectrum - Fig. 1, i) had been used for coating. It is difficult to say whether the resin had been added to wax by the painters or partial dissolving of wax took place along with its mixing with dammar when the surface was coated with varnish.

The broad band at $1600\ cm^{-1}$ in spectrum (e) may be due to the presence of resins in the sample. It is difficult to identify the green substance left after the extraction of the beeswax from the paint. Its spectrum (Fig. 1, j) is somewhat different from that of copper resinates produced of cupric acetate and colophony and other compounds (2, 3). At the same time, by means of emission spectral analysis copper was detected in this substance. It is also possible that the examined compound is not the original pigment; but a product of interaction, while the natural ageing, between the original substance, cupric acetate for example, and organic acids, in particular free fatty acids of wax.

It is apparent therefore that pure bees/wax and wax mixed with resins were employed as binding media in the examined objects. Punic wax ("Sergius and Bacchus") was used for the same purpose. On the whole this is in agreement with the traditional views on the encaustic technique.

As a result of the integrated physical and optic, as well as physical and chemical, investigation of three encaustic icons from the Kiev Museum of Eastern

and Western Art one can come to the conclusion that these icons have little resemblance in technique, which is apparently due to the fact that they had been performed at different places.

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2. Masschelein-Kleiner L., Heylen J., Tricot-Marckx F., "Studies in Conservation", 13 (1968), pp. 185-122.
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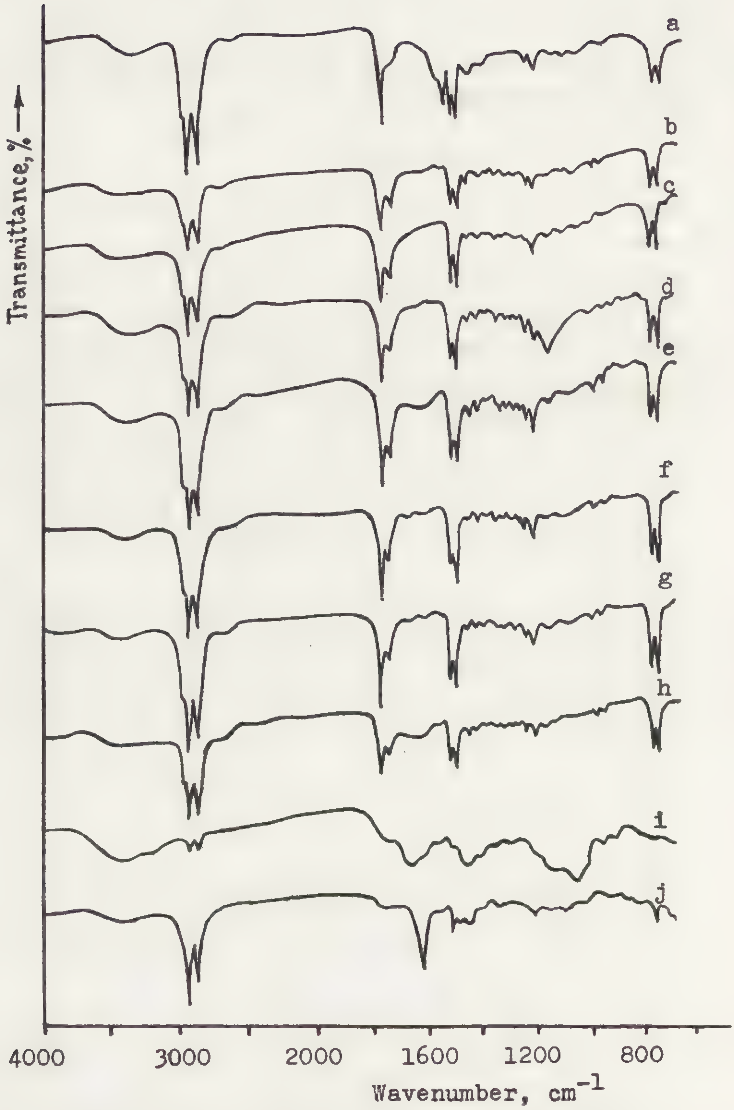

Fig.1. IR-spectra of the investigated compounds.

SILICIOUS ARCHAEOLOGICAL MATERIALS

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Programme 1975-1978

1. Bibliographie raisonnée.
2. Etude sur la technique de la dépose des mosaiques (supports, liants, protectifs, ...).
3. Etude biologique sur la résistance des adhésifs et sur le développement de la microflore sur les objets silicieux de fouille.
4. Etude chimique et physique sur les nouveaux consolidants et les nouveaux matériaux employés pour les supports et pour les intégrations des lacunes dans les matériaux silicieux.
5. Théorie et méthodologie de la restauration des matériaux silicieux.

GROUPE DE TRAVAIL: MATERIAUX SILICIEUX

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Le group de travail " Matériaux silicieux" a été creé après la réunion de Vénise. Les raisons qui nous ont poussé vers ces problèmes résident dans le fait que les objets silicieux sont les plus repandus dans les champs de fouille et dans les musées archéologiques et fournissent, donc, la plus riche contribution à la connaissance du passé. Pourtant, avec certaines exceptions, leure conservation est encore très souvent confiée à des moyens artisanaux, même si l'on dispose d'une vaste gamme de nouvelles techniques et de nouvelles matières à employer soit comme adhésifs, soit pour la protection des surfaces, soit pour combler les lacunes, soit, dans le cas des mosaïques, comme support pour la dépose. En outre les sciences sussidiaires de l'archéologie nous offrent maintenant des moyens de connaissance très avancés pour ce qui concerne la datation et la composition. C'est, donc, tout un nouvel horizon qui s'est ouvert pour les études sur la conservation et la restauration de ces matériaux.

Pour être preparés à l'application technologique de ces données s'impose la necessité d'une recherche méthodologique. On s'est proposés d'articuler notre travail sur les points suivants:

1) Théorie et méthodologie de la restauration des matériaux silicieux;
2) Bibliographie raisonnée;
3) Etude sur la technique de la dépose des mosaïques (supports, liants, protectifs, etc.);
4) Etude biologique sur la résistence des adhésifs et sur le developpement de la microflore sur les objets silicieux de fouille;
5) Etude chimique et physique sur les nouveaux consolidants et les nouveaux matériaux employés pour les supports et pour les intégrations des lacunes dans les matériaux silicieux.

Le demarrage de ces opérations est toujours assez lent, surtout quand il s'agit de cohordonner des recherches disloquées dans le temps et dans l'éspace. Certaines études commencées n'ont pas été achevées à cause de difficultés survenues, d'autres seront presentées dans les " poster sessions " étant donné leur caractère encore _in fieri_. La réponse, il faut l'avouer, a étée inférieure à ce qu'on s'attendait. Mais dans cette circostance apparémment négative on peut reconnaître le signe de la complexité et de la nouveauté de ces recherches et, par conséquence, de l'utilité de les avoir commencées: ce qui justifie notre effort et nous pousse à persever dans ce but.

78/21/1

CONSERVATION OF ANCIENT TERRA COTTA SHERDS BY ALKOXYSILANES

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CONSERVATION OF ANCIENT TERRA COTTA SHERDS BY ALKOXYSILANES

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Abstract: In the present work some of our results on the treatment of terra cotta sherds with alkoxysilanes are presented. The method of impregnation which has been applied is described as well as the curing process of the absorbed materials. Water absorption is significantly reduced in samples treated with alkoxysilanes having water repellent properties.

Introduction

The conservation of ancient monuments is of particular importance because of their cultural significance. Due to accelerated deterioration caused by the recently increased atmospheric polution, the conservation of monuments is an urgent problem.

Studying the physical,biological and chemical processes of stone or some other materials destruction, it is noted that water is involved in almost every kind of decay[1,2]. The employed protective methods therefore should prevent water from penetrating into these materials. However no incospicuous shallow coating has been found to have a long term preservative action and occassionally it may even accelerate deterioration[1,2]. It is believed that problems associated with these treatments might, in part, be solved if sufficient penetration were occuring. In this last case an improved composite material could be formed, consisting of stone or any other material and the treating agent. The properties of composite material may, under certain conditions, contribute to the durability of ancient monuments.

In general, a successful conservation system consolidates friable material,restores or even enhances its tensile strenght and increases its water repellency. Furthermore it prevents crystallization damage by making the material more resistant to crystallization forces. This is accomplished by making salt inaccessible to water or by modifying its pore distribution[1,2].

In order to achieve sufficient penetration the treating agent should have the following properties: High surface tension,low contact angle and low viscosity at the time of application. Flammability, toxicity, vapor pressure and cost are also factors that should not be disregarded in selecting the appropriate agent[1].

Work performed in recent years has shown that in situ polymerization[1,3,4], of certain monomers is advantageous,when compared with the one in which the resin is dissolved in a certain solvent and applied to porous materials. The systems primarily employed in the first case are vinyl monomers[1,3], as acrylics[6],epoxy resins[7], stryrene - polyesters[5,8] and alkoxy silanes[2,8]. The third group of compounds will be further discussed below and some results on their application to terra cottas will

be presented.

Chemistry of Alkoxysilanes

The alkoxysilanes that have received most attention are tetraethoxysilanes, trimethoxymethyl - and triethoxymethylsilane. Tetraethoxysilane, as the scheme of reaction shows below, is hydrolyzed in the presence of atmospheric humidity, by certain catalysts, to silicic acid by the liberation of alcohol[1,9a]

$$Si(OCH_2CH_3)_4 + 4H_2O \xrightarrow{\text{Catalyst}} Si(OH)_4 + 4C_2H_5OH$$

$$Si(OH)_4 \longrightarrow SiO_2 + 2H_2O$$

Silicic acid is then converted to silicon dioxide. It is therefore possible by this treatment to introduce into the material a natural binder.

Triethoxymethylsilane and trimethoxymethylsilane are hydrolyzed forming methylpolysiloxanes, which reinforce and impregnate porous material in one operation. The methyl group of polysiloxanes is responsible for the water repellency of the material whereas Si-O linkage has a reinforcing effect. Triethoxymethylsilane is the preferred agent since its curing does not involve the liberation of toxic methanol. The loss of alcohol does not allow a complete filling of the pores and this is a serious disadvantage of the method.

In our work the alkoxysilane systems employed were produced by Wacker-Chemie ie Wacker Sandstone strengthening Agent H and Wacker Sandstone strengthening Agent OH. These materials are one-packed systems, mineral-based and are described as having very high depth of penetration, high strengthening effect and they do not attract dirt[10]. Strengthening agent H possesses water repellency properties whereas OH does not contain water repellent agents. These agents can be applied to all absorbent masonry porous material eg sandstone, limestone, ceramics.

In our experiments with terra cotta sherds the impregnating properties and curing times of H and OH systems were studied. Also, water absorption of treated objects was measured. Further work on splitting tests (based on DIN 5211) is in progress.

Application of H and OH Alkoxysilane systems to terra cotta sherds.

Terra cotta sherds utilized in our tests originate from Archanes, about 5 km from Knossos, and they belong to the Minoan era.
Terra cotta sherds were cleaned by dilute hydrochloric acid and then thoroughly washed with water. Satisfactory results were obtained although the suggested method is one utilizing the chelating properties of tetrasodium salt of ethylenediamine tetracetic acid.
This method is in current use in our laboratory.
Terra cotta sherds were dried at 105°C and impregnated in a specially contructed vacuum chamber [5b] which is shown in Fig.1. The chamber containing the samples was evacuated and subsequently H and OH were introduced under vacuum. In order to increase monomer absorption and facilitate its introduction even to the smaller void spaces, a nitrogen gas pressure was applied to the system.
Terra cotta sherds, were removed from the impregnation chamber and left to a humid area at room temperature for several days. Some samples were subjeted to a second impregnation, after the curing of the material absorbed in the first treatment was completed.

Results and Discussion.

Some impregnation data of terra cotta sherds treated with Wacker Streghtening Agents H and OH are shown in Tables I and II respectively.

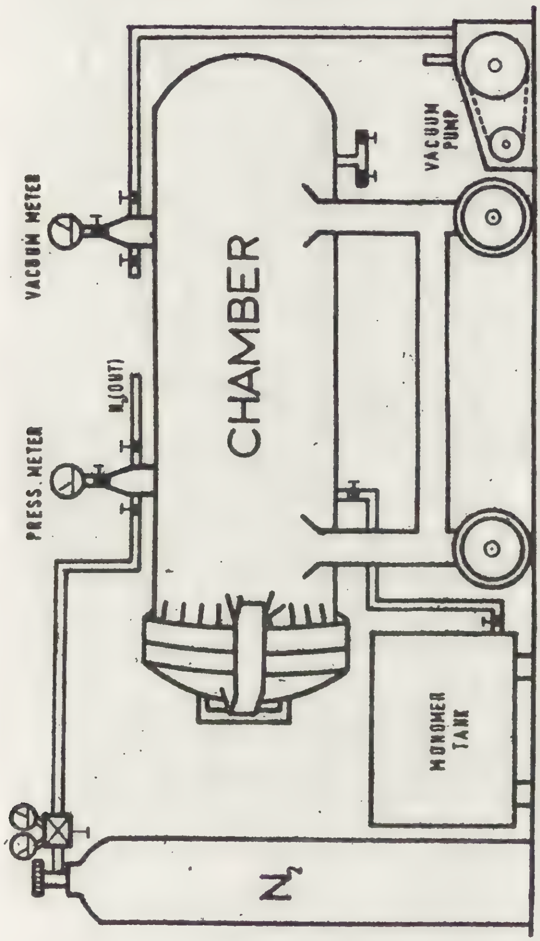
VACUUM METER
PRESS. METER
N_2(OUT)
CHAMBER
VACUUM PUMP
MONOMER TANK
N_2

Fig.8

Impregnation	Weight, gr	Sample No 31	32	33	34	35	36	37	Mean values
	Initial	15,22	6,74	5,90	6,21	6,00	5,87	6,45	7,48
1st	After Impregnation	20,13	8,78	8,06	[illegible]	8,13	7,76	8,45	9,90
	After Curing	16,92	7,36	6,55	6,85	6,68	6,50	7,07	8,28
	Increase,%	11,03	9,05	10,88	10,14	11,33	10,56	9,45	10,70
2nd	After Impregnation	20,60	8,92	8,29	8,20				11,50
	After Curing	18,20	7,83	7,09	7,30				10,10
	Increase,%	19,50	16,17	20,16	17,55				18,68

Table I. Impregnation and curing data of terra cotta sherds treated with streghtening agent H.

Impregnation	Weight, gr	Sample No 38	39	40	41	42	43	Mean Values
	Initial	4,70	4,82	4,24	4,25	1,71	1,81	3,59
1st	After Impregnation	6,29	5,89	5,21	5,94	2,75	2,50	4,76
	After Curing	5,31	5,22	4,61	4,92	2,12	2,09	4,05
	Increase %	12,48	8,30	8,72	15,76	23,97	15,47	12,67
2nd	After Impregnation	6,40	6,03	5,30				5,91
	After Curing	5,75	5,49	4,85				5,36
	Increase %	22,34	13,90	14,38				17,03

Table II. Impregnation and curing data of terra cotta sherds treated with streghtening Agent OH.

After first impregnation with H and OH weight increases by about 32% whereas after the second one weight increases by 22% and 17% for H and OH respectively. These last results may in some way be attributed to a specific porosity established in postsherds after their first impregnation and curing. After curing weight increases of the samples are related to the absorbed amount of alkoxysilanes. These results are summarized in table III.

		Weight increase %	
Impregnation		H	OH
1^{st}	After Impregnation	32,0	32,0
	After Curing	10,2	10,5
2^{nd}	After Impregnation	22,0	17,0
	After Curing	8,6	6,5

Table III. Weight increase % of the terra cotta sherds after impregnation and curing.

From the data on Table III it is seen that about 65% of the material absorbed is removed by the end of curing due to the loss of alcohol. This is a disadvantage of alkoxysilane treatment, as already has been mentioned.

Curing curves of terra cotta sherds treated with H and OH are shown in Fig.2. Horizontal axis refers to curing time whereas vertical to the mean percent weight decrease of the absorbed alkoxysilanes. It was found that curing is completed in about 120 hours ie in a relatively short period of time[9b]. It is clear that this is due to the great surface of potsherds which makes easier the loss of alcohol by evaporation. Hydrolysis reaction is,therefore, shifted to the right and consequently curing time is reduced.

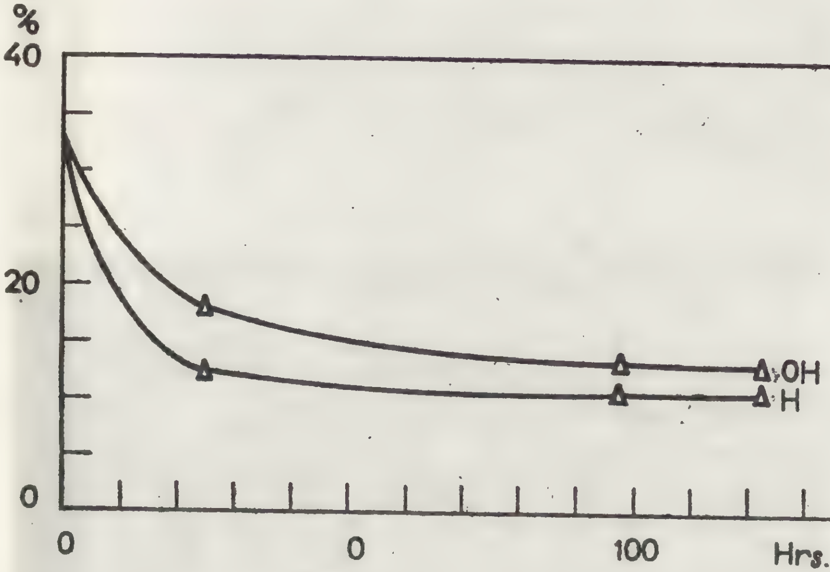

Fig.2. Curing Curves of terra cotta sherds treated with H and OH alkoxysilanes.

By the same technique, as applied to terra cotta sherds a small Minoan pottery, found near Knossos and shown in Fig. 3 was treated with OH. Impregnation was satisfactory as judged by the following results:

Pottery initial weight :	74,48 gr.
Weight after impregnation :	93,10 gr.
Weight after curing :	81,28 gr.
Weight of absorbed OH, % :	25,00
Weight increase after curing, % :	9,13

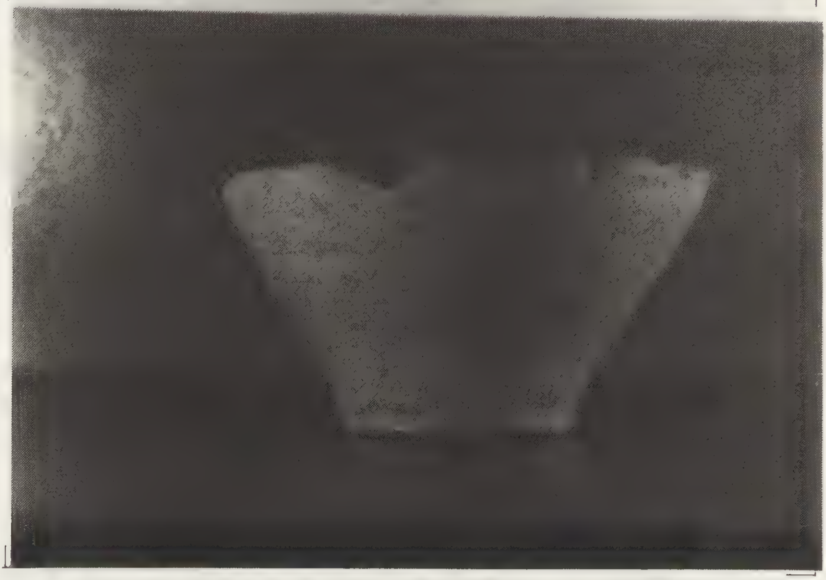

Fig. 3. Minoan pottery impregnated and cured with OH.

These results are comparable to the ones obtained in the case of potsherds where satisfactory impregnation occurs.

Water absorption in treated and untreated terra cotta sherds was measured and some results are shown in Fig.4. As expected water absorption is reduced in samples treated with alkoxysilane H. Furthermore, it was found that water absorption is almost the same with untreated potsherds and impregnated with OH.

In cured potsherds the external appearance is not affected so that one cannot distinguish between a treated and an untreated potsherd.

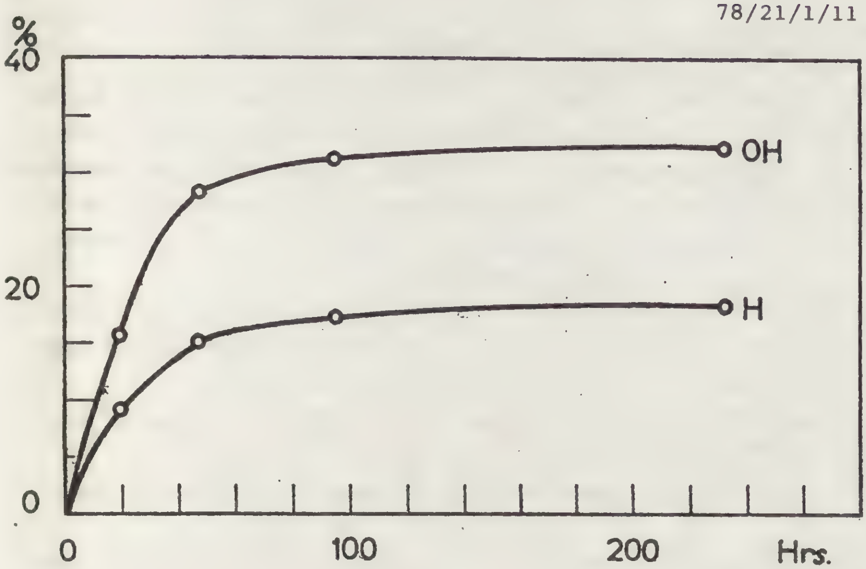

Fig.4 Water absorption data of terra cotta sherds treated with H and OH.

Further work is in progress with similar samples which will allow better evaluation of consolidation properties of H and OH before extending this conservation treatment to potteries. Comparisons will also be made with the consolidation accomplished by radiochemical methods, which are also under development in our Laboratory.[12]

Acknowledgments: The authors thank Mr.A.Antonopoulos and Miss E.Kriara for their assistance.

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A SCIENTIFIC STUDY OF VENETIAN AND PADUAN SGRAFFITO CERAMIC OF 15TH AND 16TH CENTURY

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ABSTRACT

As far as we know, Venetian and Paduan sgraffito ceramic has never been the object of detailed scientific studies. In order to contribute to the knowledge and definite identification of the various materials composing the ceramic body accurate mineralogical and chemical analyses have been done on them. To obtain information on the chemical and physical state of the iron content Mössbauer spectroscopy has been employed.

From the interpretation of the results some hypotheses on the employed technology have been drawn.

INTRODUCTION

The North Italian sgraffito pottery attribution to a certain production area is not possible by macroscopic observations or stylistic considerations about techniques, materials, forms and so on, since everywhere similar materials and decorative patterns are used by the workshops (1,2).

Attribution is immediate only when waste products or objects employed in baking indicating the nearby presence of a kiln are found together with pottery. The idenfication of the origin of most Renaissance pottery found in Venice or Padua is extremely difficult because of the lack of knowledge about its typical features. For instance, the landscape, till now considered as a peculiar motif in the Venetian area, was found to decorate also some Paduan pottery.

Undoubtedly a possible solution of the problem of the origin, date and technology, essential to a better knowledge of Renaissance pottery, can be found only by mineralogic-petrographic and chemical-physical investigations (3).

Among the analytical methods usually employed in studying pottery materials, Mössbauer spectroscopy constitues an interesting procedure to obtain information about the chemical and physical state of the iron content (4). However, Mössbauer results are seldom complete in themselves because the effect of heat treatment depends on the chemical composition and on the chemical history of the original material, as well as on baking temperature, time and atmosphere.

The possibility of using Mössbauer spectroscopy to distinguish ancient pottery materials of different provenance has already been examined with surely authenticated ware (5). Systematic differences in some spectral parameters which allow a differentiation with reasonable certainty has been found(6,7).

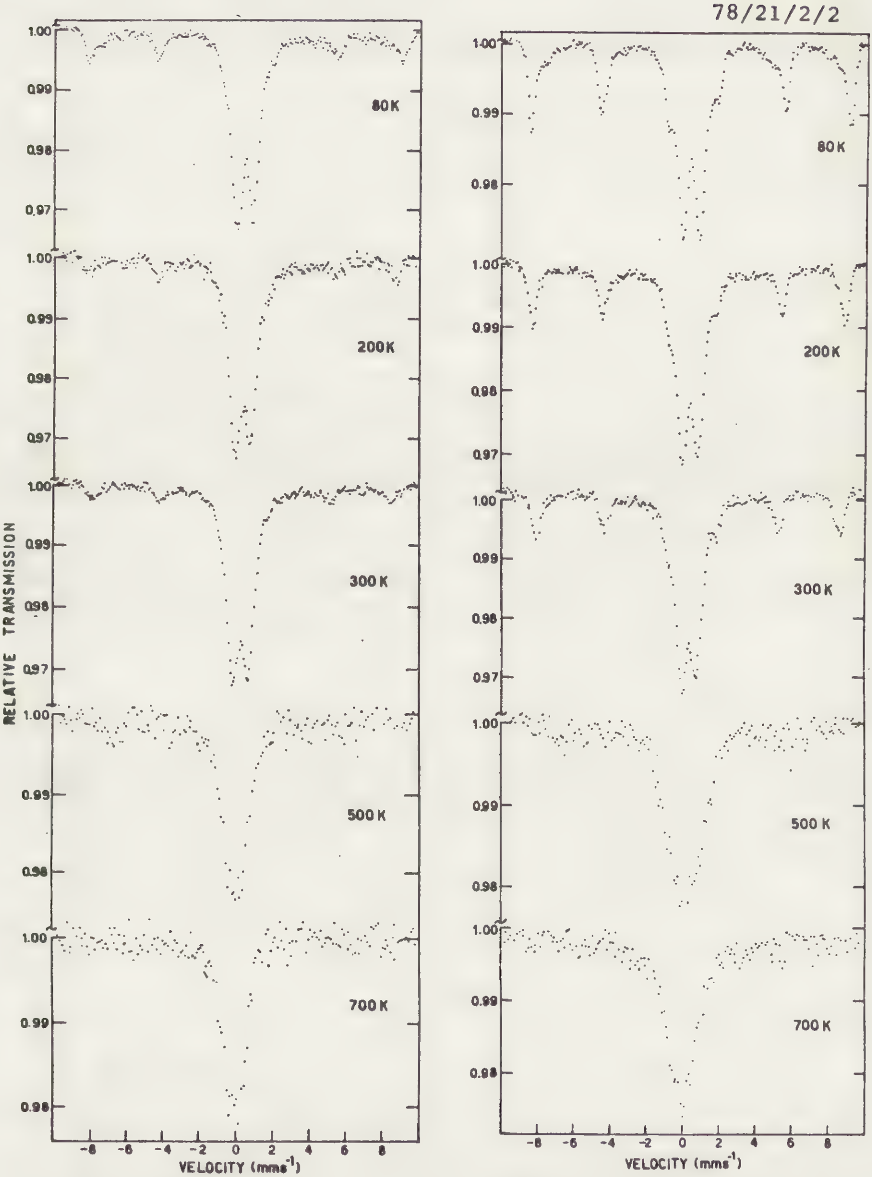

Fig.1 Mössbauer spectra at different temperatures of Venetian pottery (V13) *on the left* and Paduan pottery (P4) *on the right*.

In our work, X-ray and chemical analysis with petrographic and Mössbauer studies are carried out in order to characterize Venetian and Paduan pottery.

EXPERIMENTAL

Elemental composition analysis (Si,Al,Ti,Mn) has been carried out by X-ray fluorescence using U.S.Geological Survey standards of rocks for comparison.Iron(III) has been determined according to Riley(8),Iron(II) by means of titrimetric analysis, P,Ca and Mg according to Shapiro(9),Na and K by means of flame photometry.The ignition loss (I.L.) has been accomplished at 1000°C.

Microscopic examination in transmitted light has been accomplished on thin cross sections.Fragments presenting colour thickness or dripping have been examined on opaque cross section in order to detect traces of opaque pigments present in the glaze.

Diffractometric analysis (Cu K_α rad.at 35 kV,20 mA) has been carried out on several biscuit sample or fractions separated with bromoform and on the white slip.

Mössbauer measurements were carried out by means of a spectrometer operating in constant acceleration mode using a 100 mCi ^{57}Co(Rh) source at room temperature.The velocity scale has been normalized to a metallic iron absorber.The measurements have been performed,between nitrogen and room temperature,using a variable temperature cryostat (Oxford DN 704) and,for high temperature, a MF-Ricor furnace equipment with a digital temperature controller. A Reuther-Stokes proportional counter has been used in connection with an AME-40 Elscint spectrometer.The data points have been fitted with lorentzian components using a least-squares iteration procedure by a Univac 1108 computer.Representative Mössbauer spectra for Venetian and Paduan samples,showing experimental points in the temperature range between 80 and 700 K,are reported in Fig.1.

DESCRIPTION OF SAMPLES

The thirty-two chosen samples are surely Paduan and Venetian since they have been found together with kiln waste products and leftovers.Their origin,based on evidences of escavation is also attested by typological and stylistic criteria.

Most Paduan samples date back to the 15th Cent.during the period of the greatest diffusion of sgraffito production in Padua,while most Venetian samples date back to the 16th Cent.when this art flourished in Venice.All of them are shaped at the potter's wheel, engobed with a white slip decorated with sgraffito drawings and, with the exception of two (P15,V10),variously painted in *ferraccia* yellow,*ramina* green,manganese violet,cobalt blue and glazed.

The samples classification,description and dating are based on monographic studies (10-12).The samples,grouped according to their provenance and designated by the the letter V (*Venetian*) or P (*Paduan*) followed by a number,are briefly described here.

Fig.2. Venetian samples from V1 to V16
(top to bottom, left to right)

Fig.3. Paduan samples P2-P4 and P7-P16
(top to bottom, left to right)

Venetian Samples
(cf.Fig.2)

Fusina

V1 : potsherd of dish with three concentric circles and three Gothic letters.First half of the 15th Cent.
V2 : potsherd of plate with dry branches.15th Cent.
V3 : potsherd of basin with sgraffito leaves.Half of the 15th Cent.
V4 : potsherd of plate with animal.15th Cent.
V5 : potsherd of large plate decorated with sgraffito floral ornaments.First half of the 16th Cent.
V6 : potsherd of plate with a sgraffito bird.First half of the 16th Cent.
V7 : potsherd of plate with sgraffito geometric ornaments.Half 16th Cent.
V8 : potsherd of basin with floral ornament.Beginning of the 16th C.

Isola di Torcello

V9 : potsherd of bottom and edge of inside sgraffito dishes and with floral ornament outside.Half 15th Cent.
V10: potsherd of conventual dish with sgraffito cross and arrows. Second half of the 16 Cent.
V11: potsherd of conventual dish painted with dark *ferraccia* and *ramina*.Second half of the 16th Cent.
V12: potsherd of plate edge decorated with floral ornament.End of 16th Cent.

Isola di S.Erasmo

V13: potsherd of plate with sgraffito pomegranates.End of the 15th Cent.
V14: potsherd of plate with sgraffito floral ornament.Half of the 16th Cent.
V15: potsherd of plate manufactered by stick and style.16th Cent.
V16: potsherd of plate decorated with floral and geometric ornaments First half of the 16th Cent.

Paduan Samples
(Cf.Fig.3 for P2-P4 and P7-P16)

Via Rolando da Piazzola

P1 : potsherd of jug with geometrical ornaments.First half of the 15th Cent.
P2 : potsherd of plate with hurdle and a dotted ground.Half of the 15th Cent.
P3 : potsherd of basin wall with lozenges and leaves.Waste pottery. 15h Cent.
P4 : potsherd of basin wall decorated with lozenges and ribbon-like meander.15th Cent.
P5 : potsherd of bottom basin with poplar leaves.15th Cent.
P6 : potsherd of wall basin decorated with foliation.15th Cent.
P7 : potsherd of bottom plate with floral ornament.Beginning of the 16th Cent.

Via Tiepolo

P8 : potsherd of wall and edge of dish with pomegranates.Second half of the 15th Cent.
P9 : potsherd of wall jug with geometric ornaments. Half of the

Tab.1 Analytical data of the Venetian pottery.

PROVENANCE	SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	I.L.[a]
FUSINA	V 1	63.20	19.65	6.33	0.47	3.00	0.81	2.00	3.55	0.85	0.14	0.05	1.17
	V 2	60.91	19.30	6.63	0.30	3.00	1.42	2.42	3.58	0.77	0.13	0.07	2.03
	V 3	49.48	18.92	6.73	0.29	3.94	11.28	1.68	3.55	0.68	0.13	0.11	3.72
	V 4	50.77	20.01	7.21	0.41	4.34	10.64	1.38	3.40	0.69	0.15	0.08	1.41
	V 5	66.03	17.90	5.69	0.14	2.66	0.56	2.20	3.40	0.84	0.10	0.04	1.37
	V 6	61.87	19.93	6.67	0.34	2.92	0.72	1.95	3.85	0.85	0.13	0.05	1.08
	V 7	64.62	20.08	6.03	0.25	2.00	2.20	2.00	3.70	0.86	0.19	0.06	0.81
	V 8	53.96	18.71	5.55	0.44	5.08	8.54	1.52	3.55	0.67	0.14	0.06	1.52
TORCELLO	V 9	52.26	18.35	5.62	0.35	5.76	10.30	1.19	3.40	0.67	0.15	0.10	1.30
	V 10	59.19	17.56	6.46	0.31	3.66	6.90	1.65	3.22	0.83	0.12	0.10	0.68
	V 11	59.84	17.81	6.23	0.18	3.92	5.76	1.57	3.20	0.83	0.18	0.08	0.76
	V 12	62.40	19.22	6.40	0.17	3.28	0.30	2.08	3.82	0.85	0.11	0.11	0.32
S.ERASMO	V 13	52.94	17.81	5.85	0.34	4.84	8.10	1.25	3.70	0.66	0.22	0.05	2.04
	V 14	46.15	17.27	6.26	0.30	4.62	9.50	1.80	3.60	0,67	0.49	0.10	7.29
	V 15	49.68	17.70	5.18	0.30	4.74	10.44	2.22	3.55	0.59	0.28	0.07	7.28
	V 16	54.42	17.08	6.23	0.73	6.40	8.70	1.70	2,90	0.78	0.18	0.09	2.96

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[a] ignition loss

Tab.2.Analytical data of the Paduan pottery.

PROVENANCE	SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	I.L.[a]
VIA ROLANDO DA PIAZZOLA	P 1	58.47	19.36	6.34	0.17	3.00	4.35	1.17	4.32	0.74	0.36	0.09	1.63
	P 2	52.16	19.63	6.44	0.18	3.32	7.52	0.98	4.27	0.69	0.37	0.08	1.12
	P 3	50.05	19.96	6.83	0.10	4.80	12.50	1.16	3.77	0.64	0.28	0.09	0.68
	P 4	53.80	20.16	6.99	0.13	4.03	7.88	1.07	4.06	0.72	0.15	0.12	0.73
	P 5	57.24	18.27	6.17	0.26	3.20	6.61	1.18	3.67	0.73	0.28	0.07	3.41
	P 6	49.50	19.29	6.74	0.52	5.48	9.91	1.73	3.01	0.72	0.39	0.11	2.17
	P 7	56.80	20.32	7.00	0.32	3.53	3.64	1.35	4.01	0.77	0.21	0.08	2.16
VIA TIEPOLO	P 8	55.03	22.38	7.25	0.25	2.82	5.83	0.93	3.78	0.75	0.12	0.07	2.33
	P 9	62.55	20.75	5.55	0.21	2.28	2.54	1.16	3.90	0.82	0.20	0.09	1.61
	P 10	61.01	21.28	5.30	0.20	0.20	3.20	0.95	3.64	0.81	0.48	0.09	1.76
PALTANA	P 11	52.31	21.69	7.70	0.16	3.18	8.54	1.02	4.14	0.71	0.10	0.11	2.13
	P 12	53.83	21.44	7.15	0.24	3.82	8.46	1.02	4.02	0.82	0.10	0.10	1.04
S.CROCE	P 13	53.57	21.04	5.58	0.17	3.74	8.54	0.95	4.00	0.72	0.69	0.13	2.56
	P 14	53.80	20.16	5.50	0.19	3.38	12.60	0.83	3.40	0.68	0.32	0.06	7.86
	P 15	54.33	21.24	5.50	0.31	2.88	7.48	1.01	3.78	0.73	0.83	0.12	5.51
S.RITA	P 16	53.73	19.35	5.45	0.22	4.30	10.46	1.10	3.60	0.73	0.42	0.10	2.30

----

a ignition loss

16th Cent.

P10 : potsherd of edge plate with floral and geometric ornaments. Half of the 16th Cent.

Dumping-place of *Paltana*

P11 : potsherd of wall basin with floral decoration.Fist half of the 15th Cent.

P12 : potsherd of wall jug with a pomegranate.Half of the 15th Cent.

S.Croce

P13 : potsherd of bottom and wall of basin with little palms in squares.Waste pottery.First half of the 15th Cent.

P14 : potsherd of bottom with cuneiform arm cross and star.Second half of the 15th Cent.

P15 : potsherd of bottom dish with sgraffito star with four ends. Second half of the 15th Cent.

Dumping-place of *S.Rita*

P16 : potsherd of basin wall and edge with decorative motives.Half of the 16th Cent.

RESULTS AND DISCUSSION

a) Chemical Analysis

The percentual composition of Venetian sgraffito pottery is reported in Table 1.Small disparities are observed in the minor components:Na_2O(1.79$\pm$ 0.60),TiO_2(0.76$\pm$ 0.17),P_2O_5(0.18$\pm$0.31),MnO (0.08$\pm$ 0.04),FeO(0.33$\pm$0.40).

The remarkable homogeneity of K_2O(3.50$\pm$ 0.60),the scarce variability of Fe_2O_3(6.19$\pm$ 1.02),Al_2O_3(18.58$\pm$ 1.50),MgO(4.01$\pm$ 2.39),the remarkable variability of CaO (6.01$\pm$ 5.71),SiO_2(56.73$\pm$ 10.58) and of ignition loss (2.33$\pm$ 1.91) can be observed.

The analysis show a similarity among the data of the 15th Cent. *Fusina* specimens (V1,V2 and V3,V4) and among the 16th Cent.specimens (V5,V6 and V7). While it is possible to compare the results of the V10,V11,V12 *Torcello* samples,there is an evident similarity among the results of the V13,V16 and V14,V15 *S.Erasmo* samples.

Table 2 lists the percentual composition of Paduan sgraffito pottery.It may be observed the relative homogeneity of data for the minor components:Na_2O(1.10$\pm$ 0.63),TiO_2(0.74$\pm$ 0.10),P_2O_5(0.33$\pm$ 0.50) MnO (0.09$\pm$ 0.04),FeO (0.23$\pm$ 0.29),the variability of K_2O(3.84$\pm$ 0.83) Al_2O_3(20.40$\pm$ 2.13),Fe_2O_3(6.34$\pm$ 1.36),MgO(3.50$\pm$ 3.20),the remarkable variation of SiO_2(54.89$\pm$ 7.66),CaO(7.50$\pm$ 5.10) and of ignition loss (2.62$\pm$ 5.24).

The analysis shows a resemblance among the data of the P9,P10 samples from *Via Tiepolo*,of the P11,P12 samples from *Paltana*,of the P13,P15 samples from *S.Croce*,of the P2,P4 samples from *Via Rolando da Piazzola*.However they have different ignition losses at 1000°C.

An interesting result is the resemblance among the analysis of the minor components.If we consider that in other kinds of pottery (13) the most significant elements are present up to 20%,it is possible to state that all the samples have been made in different districts of Padua with similar materials.This is proved also by the average high lead content of glasses that causes the lightness of the glaze present in Paduan sgraffito (3).

MICROPHOTOGRAPH OF A THIN SECTION OF SAMPLE P8´:

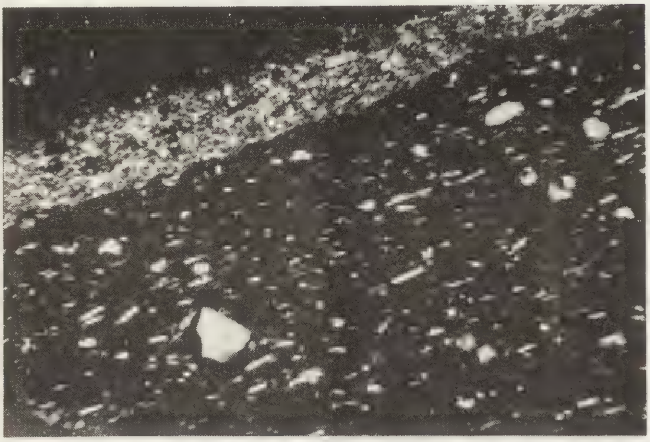

Fig.4.Crossed Nicols.46X.It shows the mullitic isorientation and the high birefringence of the white slip engobe.

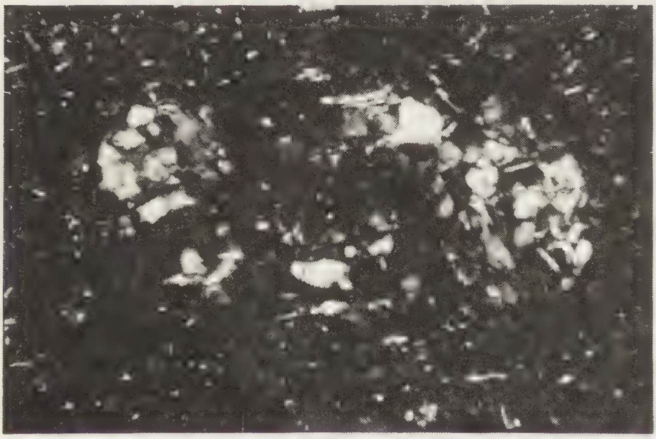

Fig.5.Crossed Nicols.46X.It shows a large polycrystalline quartz crystal.

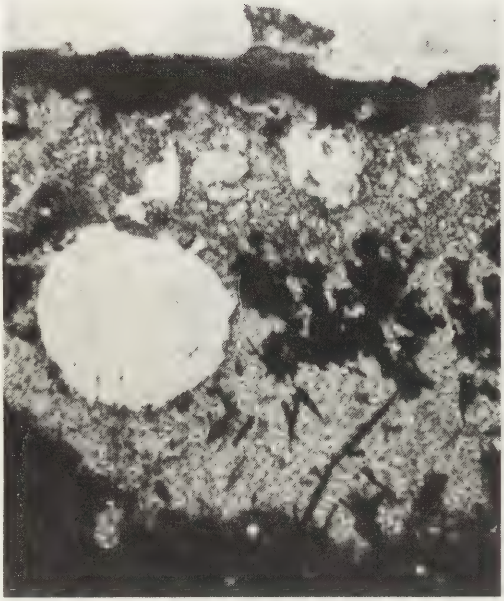

Fig.6.Crossed Nicols.88X.In the bubbly glaze several masses of opaque copper ores are evident.

b) Microscopical observation in thin section

Generally all biscuits reveal a porphiric-hypocristalline structure as in effusive rocks with a microcrystalline or vetrous groundmass and fenocrystals with a good resolution at about 100 X. The groundmass consists of vitrified minerals whose red or yellow-brown colour is due to iron oxides.

In particular it is possible to distinguish a sandy skeleton (quartz,felspar or plagioclase) and a ceramic body as a consequence of the baking process.Sandy skeleton abundance,crystalline grain, colours and mullitic growth of the examined samples are reported in Table 3.

The porosity of the Paduan samples is generally good and always greater than in Venetian biscuits.The absence of calcite nodules, responsible in pottery for breakage and ruptures during the baking is indicative of depuration and seasoning of the employed clay. The absence of fragments of silicatic rocks in the sandy skeleton means that no addition of extenders have been made to the clay.

A constant in the fabric is the remarkable isorientation of mullitic crystals (Cf.Fig.4) especially in thin biscuits (dishes, cups) and the less remarkable isorientation in large objects(jugs and basins).In fact if mullite and quartz crystals are present in elongate shapes they settle parallely to the edge of the ceramic object.This is at the basis of the typical lamination effect (14) noticeable in pottery and is due to the turning of the potter's wheel.The orientation of the mullitic needles(15) depends on disposition in the original clay material,especially kaolinite.

As it is well known,the mullitic growth is a typical thermic index:the highest is the baking temperature,the greater is the growth of the mullitic crystals.On this ground,we can say that Venetian pottery are baked at higher temperature than Paduan pottery.

In all biscuits there are many deep-red or brown nodules or inclusions often vitrified and isolated from the body.The examined fragments show a uniform composition.The following minerals are present in the ceramic body:

QUARTZ : in small crystals showing a concoid fracture and,often, a wavy extinction and corrosion traces along the edges.They are rarely in polycrystalline masses of detritic origin (Cf.Fig.5),and show needle-like inclusions.

MULLITE: is present in colourless or slightly yellow isorientation needles with a low pleochroism.The largest crystals show characteristic(010) cleavage an the right extinction.

FELSPAR: in altered,brownish masses or fractured crystals.

PLAGIOCLASE:in twinned crystals with Albite or Albite-Carlsbad laws, of albite - oligoclase composition.

IRON OXIDES and OPAQUE MINERALS:they are abundant in small masses or spreadings probably of limonitic or haematitic composition.

PYROXENE:rather rare.If present,it exhibits small crystals of globular form.It is more abundant in Venetian ceramics.

The white slip in most cases shows a porfiric hypocrystalline structure made of colourless,small straws and masses sometimes assuming a mosaic disposition.Several quartz crystals and opaque particles can be observed in this high birefractive layer.In some sections also mullite lamellae are present.The slip of some other samples

shows a mosaic structure of quartz crystals.The thickness of the slip varies from 0.06 to 0.40 mm,with an average value of 0.13 mm for Paduan ceramics.In Venetian ceramics it varies from 0.08 to 0.13 mm with an average value of 0.16 mm.

The glaze appears to be tied to the slip by a thin reaction layer,opaque and very rich in bubbles.It is generally transparent and slightly coloured in yellow,green or violet in pigmented zones. This means that the pigments during the baking dissolved completely into the glaze.In several samples,however,rounded quartz crystals are present in the glaze:they probably are undissolved sand particles.In correspondence with thick coloured zones of other sections unidentified opaque minerals (perhaps the original pigment) have been observed.

The thickness of Paduan glazes varies from 0.04 to 0.40 mm ,with an average value of 0.15 mm.In Venetian glazes the variation is from 0.06 to 0.15 mm,the average value is 0.09 mm .

c) Microscopical examination of opaque sections

The ceramic body consists of the following opaque minerals:

LIMONITE : it is very abundant sometimes associated with glass in hearthy masses or in fibrous straws.

HAEMATITE : it is scarce,in small anisotropic masses,with a graysh-black birefringence.

MAGNETITE : it is rare;in white and shiny small crystals,with a strong birefringence.Crossing the Nicols,it appears as black spots.

RUTILE : it has been frequently identified in opaque sections as very small crystals with characteristic interior reflections.

In the white slip the opaques are always made of limonite while in the glaze of a Paduan sample (P8) cuprite and calchopyrite have been discovered (cf.Fig.6).This leaves the question of the use of natural minerals as pigments open.In Venetian samples only iron limonitic oxides of probably artificial origin have been identified as colouring matter undissolved in the glass.In correspondence with the sgraffito drawing it has been noticed a partial dissolution of pigments in the glazes.

d) Diffractometric analysis

The Venetian and Paduan biscuit diffractograms are quite similar and show the presence of quartz,felspar or oligoclase.A Paduan (P3) has shown the mullite peaks which in other diffractograms have been masked by qurtz(16).In order to confirm the presence of mullite in the other samples,a separation of quartz and felspar from mullite has been carried out by means of bromoform.

The diffractometric analysis of the heaviest components has shown typical mullitic peaks,corroborating thus microscopic observations.Diffractometric analysis has shown that the engobe set apart from the *bianchetto* scratched from the P15 and V10 samples consists of quartz and illite.This result is in agreement with the final baking products of illitic kaolin and justifies a probable Vicentine origin (perhaps Tretto) of the engobe.

Tab.3. Hand and microscopical characteristics of the ceramic body.

SANDY SKELETON	High abundant	Average abundant	Low abundant
	V1,V2,V4,V5,V6,V7,V10 V11 P5,P6,P7,P15	V8,V12,V13,V15 P1,P4,P9,P10,P12,P14, P16	V3,V9,V14,V16 P2,P3,P8,P11,P13
CRYSTAL GRAIN	Average - to Large	Small	
	V1,V2,V5,V6,V11 P1,P4,P5,P6,P7,P9,P10, P11,P12,P14,P15	V3,V4,V7,V8,V9,V10, V12,V13,V14,V15,V16 P2,P3,P8,P13,P16	
COLOÜR	Red	Light Brown	
	V1,V2,V5,V6,V7,V10,V11, V12,V13 P1,P2,P4,P5,P7,P9,P11, P14	V3,V4,V8,V9,V14,V15, V16 P3,P6,P8,P10,P12,P13, P15,P16	
MULLITIC GROWTH	High	Low	
	V1,V2,V3,V4,V5,V6,V7, V10,V11,V12,V13,V14,V15 P1,P5,P8,P9,P10,P11,P12, P15	V8,V9,V16 P2,P3,P4,P6,P7,P13, P14,P16	

Table 4.Mössbauer parameters of Venetian and Paduan pottery (δ,2ε,LW are in mm s^{-1},H in kOe).

SAMPLE	TEMPERATURE (K)	NON MAGNETIC COMPONENT $\delta^{a,b}$	Δ^{b}	LW^{b}	R^{c}	MAGNETIC COMPONENT $\delta^{a,b}$	$2\varepsilon^{b}$	LW	H_{eff}^{d}	P^{c}	MAGNETIC IRON / TOTAL IRON
V 4	80	0.35	1.00	0.82	2.8	0.47	0.17	0.45	496	0.5	0.42
	200	0.32	0.87	0.91	2.5	0.47	0.20	0.72	514	0.2	0.11
	295	0.23	0.84	0.80	3.5	0.39	0.25	0.66	501	0.3	0.10
V 5	80	0.38	1.06	0.86	1.4	0.52	0.11	0.50	527	1.8	0.61
	200	0.31	0.97	0.78	1.8	0.48	0.16	0.60	517	1.4	0.55
	295	0.26	0.89	0.68	2.0	0.43	0.23	0.58	503	1.1	0.52
V 7	80	0.31	0.96	0.81	0.1	0.44	0.16	0.58	520	0.5	0.62
	200	0.23	0.95	0.84	0.5	0.42	0.19	0.60	510	0.4	0.54
	295	0.13	0.83	0.92	0.5	0.35	0.24	0.58	493	0.3	0.53
V 10	80	0.41	1.14	0.82	2.5	0.54	0.06	0.68	523	1.1	0.42
	200	0.37	1.11	0.82	2.4	0.50	0.14	0.68	515	0.8	0.38
	295	0.30	1.08	0.68	2.1	0.45	0.24	0.72	500	0.6	0.36
V 12	80	0.39	1.21	0.90	2.1	0.53	0.12	0.58	524	1.4	0.45
	200	0.33	1.09	0.92	2.1	0.48	0.11	0.66	514	0.9	0.38
	295	0.26	1.03	0.84	2.1	0.43	0.20	0.66	501	0.7	0.36
V 13	80	0.30	0.88	0.70	2.8	0.47	0.13	0.74	518	0.5	0.27
	200	0.26	0.85	0.78	2.7	0.42	0.24	0.54	512	0.3	0.18
	295	0.23	0.83	0.78	2.7	0.40	0.25	0.82	494	0.2	0.14
V 16	80	0.34	0.88	0.68	3.1	0.54	0.16	0.56	519	0.5	0.22
	200	0.31	0.85	0.70	3.1	0.52	0.30	0.66	504	0.4	0.20
	295	0.30	0.83	0.74	3.1	0.52	0.33	0.78	488	0.3	0.18
P 4	80	0.39	0.93	0.70	2.4	0.53	0.16	0.48	525	1.3	0.43
	200	0.33	0.88	0.76	2.6	0.50	0.20	0.46	517	1.0	0.33
	295	0.22	0.80	0.76	2.7	0.40	0.21	0.54	501	0.8	0.32
P 7	80	0.34	0.95	0.94	0.7	0.47	0.18	0.96	488	0.2	0.43
	200	0.31	0.91	0.90	0.7	0.63	0.30	0.86	479	0.1	0.15
	295	0.24	0.81	0.92	0.7	0.49	0.23	0.84	476	0.1	0.06
P 8	80	0.29	0.86	0.66	3.2	0.41	0.12	0.56	524	1.3	0.41
	200	0.25	0.85	0.70	3.1	0.41	0.15	0.58	514	0.9	0.31
	295	0.19	0.81	0.70	3.0	0.39	0.20	0.64	499	0.7	0.29

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[a] relative to iron metal at room temperature; [b] < 0.06 mm s^{-1} ; [c] relative intensity(%) ; [d] $\pm$ 5 kOe

e) Mössbauer measurements

Mössbauer parameters: isomer shift(δ), quadrupole splitting(2ε), line width(LW), magnetic field (H_{eff}) and the relative intensities (R%) at 80,200,295 K of ten of the thirty-two Venetian and Paduan studied samples are reported in Table 4. All isomer shifts are relative to iron metal.

Typical Mössbauer spectra consist of a superposition of a quadrupole doublet and a six-line pattern. Differences in the relative intensity of the two components are observed: at room temperature, the relative intensities for the non magnetic and the magnetic component are 2.0 and 1.1 for V5 sample and 0.7 ,0.1 for P7 sample. As the temperature decreases, the relative intensity of the magnetic component is always enhanced and the line width decreases (cf. Table 4) because of the superparamagnetic contribution of small α-Fe_2O_3 particles. At 700 K the spectra collapse to a single line (cf. Fig.1) without magnetic feature.

All spectra exhibit hyperfine magnetic field values smaller than for a pure α-Fe_2O_3. The greater line width of the magnetic component may be connected with the presence of different sizes of α-Fe_2O_3 particles. The smaller magnetic field may be due to substitution of iron(III) by aluminium(III), $(Fe_{1-x}\,Al_x)_2O_3$.

The approximate variation of the H_{eff} with the rate of substitution (x) has been studied by Janot's relation (17). The rate of substitution is in the range 11-16% but for the samples V7, V13, V16 and P7 the reduced magnetic field can be explained by the presence of the substitutional impurities other than aluminium(III) and by vacancies.

Mössbauer spectra of P4, P7, V4, V13, V16 samples present also low intensity six-line patterns probably due to Fe_3O_4 traces.

The central doublet may be considered as a superposition of the paramagnetic structural ferric component in the lattice and of the superparamagnetic small particles component. The peaks of the central doublet are rather broad which is probably due to a lack of resolution and in the sample V16 and in the Paduan samples to partial contribution of iron(II). The iron(II) presence in the Mössbauer spectrum of the V16 sample may be explained by its chemical analysis (cf. Table 1). All iron(II) traces have disappeared from Mössbauer spectra of samples heated in the atmosphere at 700 K (Cf. Fig.1).

Differences in the ratio of magnetic area to total area of Mössbauer spectra are observed among the examined samples (cf. Tab. 4). At 80 K, for example, the ratio is about 0.4 except for V5, V7 (0.7) and for V13, V16 samples (0.2).

The magnetic iron/total iron ratio increases as the temperature falls (cf. Table 4) since the magnetic component increases to the detriment of the paramagnetic component.

On going from room to nitrogen temperature the increase is in the range 0.04-0.12 except for V4 (0.32) and P7 (0.37).

CONCLUSION

Mineralogical and chemical analyses prove that Venetian pottery was made in kilns placed in several districts of Venice.The kilns utilized clay extraced from several area of the Lagoon.This agrees with some ordinances of the 15th century of the Venetian Senate(18) regulating clay quarrying.Moreover the results of the analyses point to Battaglia area mentioned by Piccolpasso(2) while it is improbable the Venetian supply of *terra* of Ravenna,Rimini and Pesaro.

The chemical analysis results of the 15th-century and 16th-century samples (cf.Table 1 and 2) show a SiO_2 increment ans a CaO decrement on going from the 16th century to the 15th century samples. Moreover Paduan clay is rich in P_2O_5,CaO,Al_2O_3 but poorer in MgO and Na_2O than Venetian clay.

From a macroscopic point a view,the Venetian biscuits show a small crystal grain indicating the use of more compact clay having a smaller detritic content than Paduan clay.Probably the more compact structure depends from longer seasoning and from clay threshing treatments before use.The better mullitic growth in Venetian pottery seems to point to a higher baking temperature (980-1000°C).

The greater pyroxene quantity in the Venetian biscuits is probably connected with clayey sedimentation basin of the Lagoon which in those times was affected by the contributions of several rivers as Piave,Brenta,etc.

X-ray diffractograms of the ingobe indicate the same origin of the employed kaolin confirming the use of the *terra* of Vicenza by the Paduan and the Venetian ceramists.

If the chemical analyses relative to iron(II) are considered a greater reduction of Paduan clay(0.23$\pm$ 0.29) (cf.Table 2) in comparison with Venetian clay (0.33$\pm$ 0.40) (cf.Table 1) may be inferred.Mössbauer spectra do not reveal a significant iron(II) presence as a consequence of oxiding atmosphere in the firing technique.Conversely they confirm the smaller oxidation of Paduan pottery in comparison with the Venetian pottery as a consequence of lower baking temperature or of partial clay reduction during firing.

The variation of the magnetic iron/total ratio (cf.table 4) at various temperatures is a clear evidence that a distribution of α-Fe_2O_3 particle size is present. The differences in the ratio of the magnetic area to the total area are connected with the nature of the clay baking processes because the higher firing temperature results in an increase in particle size and in a trasformation of the structural iron into oxide form.

This magnetic iron/total iron ratio and the related paramagnetic iron/total iron ratio may differentiate Paduan pottery from Venetian pottery and may also provide a valid criterion in dating them.

Mössbauer measurements of the whole set of samples are still in progress to verify if the distribution of the values for the quadrupole splittings of the central components,iron(II) and iron(III) and the paramagnetic iron/total iron ratio for α-Fe_2O_3 show systematic differences.

This preliminary communication is meant to demonstrate that,also for relatively modern pottery,Mössbauer spectroscopy gives a considerable amount of information.

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SOME PROBLEMS CONCERNING REPEATED RESTORATION OF ANTIQUE PAINTED VASES

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SOME PROBLEMS CONCERNING REPEATED RESTORATION OF ANTIQUE PAINTED VASES

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Soviet museum collections of antique painted vases include a number of specimens restored as early as the end of the 19th and the beginning of the 20th century, by application of the so-called "antiquarian" technique. Similar vases can be found in museums of other countries /1/. To the unaided eye they usually seem to have their pristine appearance and it is only rarely that an apportunity presents itself to discover that it is not so. The thing is that "antiquarian" restoration was performed according to the then popular method (in fact, it had been popular until the twenties) - the so-called "substitution" technique.

The basic idea was that a decayed object should look, when it had been restored, like new. To achive that goal some specific restoration methods had been applied, which came to light only after several such objects had been restored for a second time.

"Substitution" technique includes the following procedures:

1. Fragment selection and pasting. The following adhesives were used: lime mastics, water glass and the so-called Mendelyeev's putty (a mixture of rosin, mummy, yellow wax and linseed oil).

If, after the application of adhesives some fragment projected by one or two millimeters it was ground off with the result that its surface and, consequently, the design were destroyed. Sometimes in order to get rid of the defects caused by thick joints edges of pie-

ces were ground off and the space between the fragments was widened.

2. Substitutes for missing fragments were usually made of gray calcined clay. They were replicas of missing piecies, e.g. sides, legs, handles and necks; after being modeled they were calcined and their edges were ground off so that they could fit the lacunae, after which they were pasted together with the original pieces. Sometimes missing fragments were substituted by fragments of other antique vessels.

3. Then the joints were plastered and coloured so thoroughly that it is often impossible to suspect that the vessels have a fragmentary structure. Finally, to conceal all the traces of restoration the vases were repainted.

Sometimes the whole of a vase was repainted. For this purpose its surface was coated with a thin layer of mastic - a mixture of glue and chalk. The plaster was coloured with orange-brown paint similar to clay in hue, over which a design was made, in the red-figure style, which was a fairly good imitation of the original drawing; the latter, however, was completely concealed under the new painting. In most cases new drawings coincided with old ones, but a vessel has been found with a detail that had not been there originally, but was added by the restorer.

Sometimes an original drawing was partly preserved and only joints were repainted. But in those cases, too, restoration painting went over onto the main surface in order to efface the discrepancy in colour and condition between the new and the original painting.

In one case a missing part of an Attic scythos of the 5th century B.C., performed in the red-figure style, was replaced with a fragment of a later red-figure style vessel.

4. Sometimes a finishing touch was given to vases by coating them with cellulose nitrate varnish - a fact which allows to determine the date of restoration as the beginning of the 20th century, that is the time when this first synthetic lacquer was invented. Some vases were totally varnished. In that way defects of vessels performed in the red-figure style, such as worn spots and scratches, were concealed.

Under the action of light the varnish layer had darkened corrupting the original colour and giving it a dingy greyish tint. It was that made me suspicions when I examined a crater of the 5th century B.C. performed in the red-figure style, with a drawing representing fighting warriors wearing high conical pyloses and Corinthian helmets. My supposition was confirmed when the crater had been examined in ultraviolet rays. The varnish luminiscented intensively over the whole surface; the effect has been photographed.

The proposed repeated restoration technique includes the following principal stages:

1. Selection of the objects to be restored begins with visual inspection and technical examination. Technical examination involves an examination of an object in reflected ultraviolet rays with the aim to determine (or to confirm the results of visual inspection) the presence of a varnish layer. The original painting concealed by the first restoration is then disclosed by means of infrared rays.

2. Restoration painting and varnish coating are removed with dymethylformamide. After that the vessel is washed with water and dried.

3. As a rule, vessels are never completely disassembled because it is rather difficalt to remowe the adhesives that were used (lime mastics, water glass). The only possible way to remove then is a mechanical

treatment which is bound to lead to further damages. However, a vessel may be partly disassembled in order to eliminate pasting defects.

4. If needed, substitutes for missing fragments may be performed in clay, according to the "direct" analogues available. In one case the neck, handles and a leg of a vase turned out to be parts of several other vases. The curators had been consulted and the decision was taken to leave those fragments intact after removing the restoration painting.

5. One of the most debatable questions, - not only in ceramics restoration, but also in restoration as a whole - is whether plaster substitutes should be coloured.

Some restorers leave plaster uncoloured, some prefer to colour plaster in tone, similar to the original, but slightly lighter or darler, others mask the differencies between the original fragments and plaster substitutes by way of imitation colouring, there are even some who venture missing parts of drawings and ornaments /2/.

I have no intention to support the "antique" restoration colouring technique. That the above-mentioned methods of colouring co-exist nowadays is due, perhaps, to the fact that different ceramic objects can belong to different categories, moreover, one object can belong to two categories. Antique painted vases provide an excellent example.

Being archeological objects they can be regarded as "historical" monuments. At the same time these vases are samples of Hellenic drawing /4/ and as such should be included into the category of works of art.

Since, as is well-known, each category requires specific methods of restoration the limits to which an

object should be restored are defined differently for each category.

A "historical" monument is, above all, a scientific document, so the new elements introduced in the course of restoration should be clearly distinct from the original ones. That idea served as a cornerstone for a new technique - the so-called "archeological", or "analytic" method - which succeaded the "antiquarian" technique in the twenties. The method was used by V.D.Blavatsky, an archeologist and historian of the antiquity, in clearing antique painted vases from the State Museum of Fine Arts collection. In particular, a signature of Polygnoth, a well-known Greek vase painter, was discovered on one of the vases.

Restoration painting was removed from many vases and joints were cleared of putty, which accentuated the fragmentary structure of the vessels. No further restoration work was done.

However, to do so is, to use I.Grabar's apt expression, to fall into "snobbery of fragmentarization". One should always bear in mind that antique painted vases are artistic works as well.

Consequently, it seems a good idea to colour only substitutes and joints without affecting the main surface; hue should be similar to the original one, yet slightly different; those parts of the general conteur of a drawing about which there are no doubts may be reconstructed, but repainting details should be avoided.

An object thus coloured preserves its aesthetic integrity.

All new elements introduced in the course of repeated restoration should be entered in a restoration record where a detailed photo-documentation and description of restoration processes must also be presented.

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TRAINING OF RESTORERS

Coordinator : K.E. Holm (Denmark)
Assistant coordinator: P. Cannon-Brookes (U.K.)
Members : N. Baer (U.S.A.)
Y.O. Dawodu (Nigeria)
G. de Guichen (International Centre for Conservation, Rome)
H. Hodges (Canada)
H. Jedrzejewska (Poland)
C. Pearson (Australia)
G. Petit (France)
I. Sandner (G.D.R.)

Programme 1975-1978

1st year: To collect information about existing training programmes, on the basis of the inventory now established by the International Centre for Conservation (Rome).

Members of the group will assist in procuring relevant information from their part of the world.

2nd year: To analyse the programmes and compare them.

Members of the group will be given different tasks in connection with the comparison. They may ask for additional information at this phase, for the sake of completeness.

To define the different tasks, which could be given to different members of the group, must await the analysis of the procured material. The first analysis will be done by the coordinator and the assistant coordinator, who will thereafter make suggestions to the rest of the group.

3rd year: The group will prepare reports for the 1978 meeting.

Along with this survey, it should be possible, to gather information about didactic material available: literature, slides, films, etc. and about training centres, which could accept students on an exchange basis - and finally about teachers, who might act as travelling professors.

78/22/1

CONSERVATION TRAINING AT GATESHEAD - THE PAST TEN YEARS

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CONSERVATION TRAINING AT GATESHEAD - THE PAST TEN YEARS

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ABSTRACT

The course for the Gateshead Diploma in Conservation of Paintings started in 1967 with practical training in conservation of easel paintings and now offers an alternative option in conservation of prints and drawings. The content of the two-year course and method of student assessment are described. Future developments include the possibility of extension to a three-year course to allow for expansion of academic subjects, opportunity for students to continue specialisation in one option but to have some practical experience of the alternative option and to give time for museum attachment. The majority of students are graduates but some younger, non-graduate students are included. Good experience with such students at Gateshead confirms that there is place for non-graduates together with graduates on the same formal course in conservation training.

Training in conservation of paintings started at Gateshead in 1967 when Mr Wilfred Taylor, picture restorer at the Shipley Art Gallery accepted three trainees. In 1968 the teaching base was transferred from the Art Gallery to Gateshead Technical College close by so that the students should be eligible for financial aid from their local Education Authority. Teaching staff, students and equipment were moved to a self-contained, nineteenth-century house in the grounds of the College which is still used solely by the Conservation Department.

Student numbers for the two-year diploma course gradually increased until there was an intake of eight students each year. In 1974 it was necessary to take twelve new students to satisfy the requirements of the Department for Education and Science and a decision was made to offer two options in the course so that eight students specialise in conservation of easel paintings and four students specialise in conservation of prints and drawings each year. This has continued and there are now five full-time members of staff with

a maximum of twenty-four students.

The two-year course has a strong practical element; approximately 66 per cent of a student's time is spent in practical conservation in the first year and 70 per cent of the time in the second year. The remaining time is spent on academic subjects, including chemistry, physics, art history and study of materials and techniques, that all students take together in the first year regardless of specialisation. Print-making is taken in addition by the students specialising in prints and drawings. These subjects are taught by other staff either within Gateshead Technical College or at Newcastle Polytechnic. In their second year students take chemistry in two separate groups according to their specialisation; they also continue with print-making and, in a combined group, with the study of historic techniques.

Qualifications for entry to the course are a University degree, an art school diploma or two General Certificate of Education 'A' levels, one of which should be art and the other a science subject. No student is accepted under eighteen years of age. At interview all candidates must show evidence of draughtsmanship and colour sensitivity, usually in a portfolio of drawing, painting, printing or photography. A slide test is given to examine a candidate's observation and knowledge of art history. A practical test may also be set.

At the end of the first year, assessment is based on written examinations in chemistry and physics with a practical test in chemistry, a tutor's assessment of practical work in conservation, painting or print-making, and an oral examination which includes a slide test. A student failing any of these subjects must repeat the examination successfully before proceeding to the second year. Final assessment at the end of the course includes submission of complete conservation documentation for the final year's work, a tutor's assessment of practical work throughout the year, a general written paper that includes questions on conservation theory, chemistry and history of materials and techniques, and an oral examination and slide test. An external examiner marks the written paper, examines each candidate's documentation in conjunction with the practical work that has been carried out and then conducts the oral examination with members of the College staff. Assessment of a student's work in practical conservation forms 60 per cent of the final grade, while performance in the written paper and the oral examination each account for 20 per cent of the total mark. Successful students are awarded the

Gateshead Diploma in Conservation of Paintings. The external examiners come from two of the national museums in London.

Opportunity exists for some students to study for three years, taking two years in one option and a third year in the alternative option. Having already completed those parts of the course taken by the combined group in first and second years, a student in the third year spends a very high proportion of time in practical work. Three students have recently completed three years' study.

Having outlined how the course has developed over the past ten years, it is worth considering possible future developments.

Extension of the course to three years is under active consideration. Despite the fact that students at Gateshead possibly accomplish more practical work in two years than those participating in similar University-based courses in the United Kingdom owing to the considerably longer academic terms at the Technical College, it is generally felt that the students would benefit from three years of study. It would be our intention to provide time for expansion of academic subjects, for work in the alternative option and for museum attachment. Extension of academic subjects would include art history and study of materials and also provide a practical painting course on similar lines to the print-making course already included. (At present, students specialising in easel paintings practise painting in egg tempera and gilding but on a somewhat individual basis rather than in a formal group). Availability of more time would provide opportunity, probably in the second year, for students to participate in practical work in the alternative option. It is our intention that students would continue to specialise in one option or the other, since techniques of restoration for easel paintings and works of art on paper differ. However, as both disciplines are practised in the same department, it is recognised that students should benefit from the opportunity to gain some experience of problems and techniques outside their specialisation.

Work on location has been included from time to time, often at the end of the summer term, but extension of the duration of the course would make this very much easier. Furthermore, with the steady growth of conservation in North East England in recent years, museum attachment under professional conservators is becoming a more practical proposition.

At this point it is worth emphasising that the relationship between those responsible for the College course and surrounding museums and galleries is excellent. In 1977 works of art for conservation treatment came from the Bowes Museum, Barnard Castle, five museums in Tyne and Wear, from Carlisle, Hartlepool and Whitby through the Area Museums Services, from Newcastle Cathedral and a church in Northumberland, from Newcastle and Durham Universities, the Royal Scots Dragoon Guards at Catterick and the Shuttleworth Collection in Bedfordshire. The last named has, for three years, provided opportunity for students to undertake first-aid work on location, while the Conservation Department of Tyne and Wear Museums has provided vacation work for a number of students. Travel for work on location, conferences and museum visits is assisted by a grant from the Leverhulme Trust.

In the long term, future plans must include some expansion in studio accommodation. The course is still based in a self-contained house in the College grounds with eight restoration studios, a photographic studio, dark room and radiography room. Following pressure on studio space after the introduction of conservation of prints and drawings, there is no longer a lecture or study room in the house nor a room for microscopy and chemical analysis; such activities must take place elsewhere. A second dark room and a varnishing room are also needed. Space is available for an extension to be built on to the house and if funds become available, this is likely to be undertaken. However, looking into the future, if a regional conservation centre were established in the vicinity with sufficient studio accommodation, some practical elements of the course might be removed there. Modern, purpose built premises would certainly benefit the course.

Change from a College diploma to a national award in conjunction with another, degree-giving institution has been discussed, but the additional status this might confer would possibly be nullified by academic requirements for greater emphasis on theoretical subjects at the expense of practical work. This would be unacceptable, as the Gateshead course has always been and is likely to remain an intensive training for practising conservators. At variance with opinion in North America where it is generally considered that conservation training should be postgraduate in nature and should merit a Master's degree, it is probably true to say that the general feeling in England is that conservation training may be postgraduate in nature but that practical performance and experience count for more than a further degree. At present, all training courses in conservation of easel paintings and prints

and drawings in England offer a diploma as opposed to a degree.

The Gateshead course is the only one of the three academic institutions in England offering training in conservation of easel paintings that is not University based and does not insist on students having a degree. In practice, however, the majority of students training in conservation at Gateshead are graduates; in 1977 eleven out of twelve candidates awarded places were graduates although ultimately only eight graduates took up places as some of the others failed to obtain a financial grant.

It seems likely that Gateshead will always have a few younger, non-graduate students and that we shall continue to offer the opportunity for conservation training to some candidates who cannot meet entry requirements demanded by some of the other training centres. It has been our experience that a number of the eighteen and nineteen year old non-graduate students we have had have been highly motivated and extremely hard-working on both the practical and academic elements of the course. Some such students have decided upon a career in conservation as early as fourteen years of age and have consequently studied necessary background subjects by the age of eighteen or nineteen, an age at which they are still receptive to a learning situation and their enthusiasm is easily directed. Two of these students have taken advantage of the opportunity to take a three-year conservation training at Gateshead and both are now employed in conservation of prints and drawings.

Some other very successful students come to us after spending two or three years in commercial restoration. Whether graduates or not, they have already proved a genuine and lasting interest in conservation and, without exception, they make good progress with practical work, are ready to try out different methods and concentrate well on conservation theory and academic subjects, as the need for those subjects has usually prompted them to enrol on a formal course in the first place. Having had experience of conservation trainees in Canada and England, I am convinced that emphasis on the necessity for conservation training to be at post-graduate level, as in North America, is rather unnecessary and that there is room for graduates and non-graduates on a diploma course in conservation. All must be carefully selected but, as long as the non-graduates complete both practical and academic elements of the course satisfactorily, they have the potential to make just as good restorers as graduates with similar length of conservation training. They are

probably less likely to become conservators who conduct research but they will make responsible and informed decisions and carry out work that needs to be done.

Having students of varied background on the course is successful in our view, not only judging from our teaching experience but also taking into account the employment record of students trained at Gateshead. Twenty-eight are now working in museums and galleries in the United Kingdom and three are working overseas. A few of these proceeded to further training at Stuttgart, Zurich or Brussels before taking up employment. Another twenty-four are working in commercial restoration and three are teaching. It must be recognised that over the past ten years, Gateshead has provided practical training, the success of which may be judged by the subsequent performance of the majority of its past students.

TECHNICAL MATTERS IN ART-HISTORICAL CURRICULUM

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TECHNICAL MATTERS IN ART-HISTORICAL CURRICULUM

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ABSTRACT : Considered are the basic arguments for the introduction of technical matters into art historical studies. Comments are given on particular factors that may influence the final effect of such teaching. This includes problems of the duration of the course, the proper selection and presentation of material, the proper teacher, and the program itself. The paper is based on the author's own experience in this field.

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It is our moral obligation to preserve the existing cultural heritage of mankind for future generations. But what is important in these relics? What should be preserved? Who is supposed to take care of this?

Objects coming from the past are historical documents. At the moment of creation their original features were determined by three factors: the substance, the shape(design) and the "touch of the maker's hand". They represented the original human thought and intentions. To this, additionally, came features acquired in the lifetime. Thus, the object may bear many significant documentary values connected as well with the substance as with the "human factors". Substance serves as carrier for all this evidence. Without the human factors the object would just be a meaningless fragment of material, but without substance it wouldn't be existing at all. So, the first step towards preservation of cultural heritage is to give proper care to the substance and to protect it from natural causes of destruction as well as from harmful human interventions.

There are two different periods in the life of old objects when they are in our possession : a comparatively brief one in the conservation laboratory , and a much longer one away from the laboratory. In the first period the substance is under a professional care of the conservator but the human factors are exposed to several dangers. In the second period the object is in the hands of many different persons, often unprofessional as concerns proper care, and here it is the substance that is exposed to dangers. Thus, the second period is

in fact extremely important for the proper preservation of old objects.

Art historians,for reasons of their profession based on the existence of objects,should be more than anybody else responsible for the well-being of the cultural heritage.Extending proper protection has to be the moral obligation not only of persons officially bound to safeguard objects under their care (directors of museums, curators,custodians,inspectors,priests) but also all scholars and other specialists only occasionally having contacts with objects. Their attention should naturally be directed towards keeping objects in sound condition and protected from damage,and this in turn means,as first duty,the proper preservation of physical substance,according to principle : no substance-no object! The greatest responsibility for all this will be with the curator.He has the collection under his care.It is not only scientific research,interpretation and displaying that he is supposed to do,but ,first of all,have his attention directed towards preservation.And this fact is not always sufficiently recognized.

Protecting the physical substance calls for a certain amount of technical knowledge, of experience and of imagination to foresee the possible existing dangers and to act properly. But to act it is necessary to know.But can one know if he never was told about it? And here is something that simply seems against logic : persons that should have the greatest responsibilities in protecting objects from further deterioration are lacking even the most primitive technical knowledge needed for this task, because technical matters have no place in their art historical education.

Why must art historians remain practically "blind" to all technical matters? Why are the necessary technical subjects n o t included in regular art historical academic studies? The possible answers to these questions may be sought in the fact that art history belongs to the humanities,whereas care and protection of physical substance belong to technical sciences.These two fields are not so easily mixed,among other things, for methodological reasons. But in matters of care and protection they h a v e to be mixed for the sake of objects.It is absolutely necessary to reconcile the art historical philosophical approach to artifacts with the more technical concepts of scientists and conservators.

If the art historian is not sufficiently introduced to technical subjects he may,for example :
- not understand the requirements necessary for proper conditions of display and storage,and take at face value everything that particular specialists,engineers, etc. will suggest,

- be unable to communicate with conservators and scientists, to understand their findings and points of view, and to evaluate critically their achievements,
- give incorrect interpretations of objects if he is unable or unwilling to support this with technical evidence,
- look at cases badly needing help and not notice the fact at all,
- happily study an object falling to pieces under his very eyes,
- enthusiastically admire an obvious fake easily recognized by its technical characteristics,
- rely with absolute confidence that a conservator will always "know what to do", even not taking any interest in what is happening in the laboratory.

All this will just be a consequence of a lack of technical imagination, and of purely philosophical curriculum of art historical studies. It even happens sometimes that an art historian looks with a kind of "distaste" on these "trivial matters of substance".

On the other hand, an art historian familiar with the material problems in objects will not only be able to properly care , but also will get additional "tools" helping him and enlarging the possibilities in his studies.

So, if we agree on the exceptional moral responsibility of the art historian for guarding our cultural heritage we have also to agree that a certain amount of technical knowledge has to be included in their education. Inevitably, the art historian of the future will have to learn quite a lot about technical problems.

This is nothing new. The necessity of introducing technical matters into art historical studies has already been postulated several times /1/, but not much as yet came out of it. Occasionally, some abbreviated courses are given, mostly to museums' people, on the influence of light and humidity, on the dangers of transport, etc. But short courses will never be satisfactory as they do not cover all necessary points in the field and are too superficial and fragmentary to become deeply rooted in the art historian's memory.

Quite obviously a regular full time program of teaching is needed here to cover all relevant problems and leave enough time for more detailed considerations where necessary.

But this teaching will have to be very specific. The information will be coming from a field completely alien to the art historians' own discipline. To work at all the technical information has to be given in a way that can

be assimilated by specialists in the humanities.It has to be "translated" into art historical terms,so that a bridge connecting the two disciplines can be built and enable both specialists to meet half-way.

Very important will be here the person of the teacher.He has to be technical by basic profession but also having sufficiently long experience in the field of preservation of cultural remains.He has to be able to present problems not from the point of view of his specialty but from the point of view of the other's profession. He has to remember ~~that~~ no pure "absolute" technology will ever have a chance of being digested by specialists in the humanities.But,anyway,this technical teaching has to be done by a technical specialist. Any attempts at doing this by another art historian would result in a sad manifestation of dilettantismus.

The program of teaching will also have to be specially adjusted.It has to be on academic level but also attractive,not too heavy or monotonous.It must give the necessary technical information in the proper amount,without going too deeply into useless theories , but its main purpose should be directed towards giving the students the ability of making practical use of the acquired knowledge. So, a lot of demonstrations ,examples , experimentation,discussion of cases,etc. has to be included in the program /2/.

After all this teaching, the art historian will not be expected to become a specialist in the technical field,but only to be sufficiently acquainted with the many aspects of it.He also has to understand his limitations and not be too confident in his abilities.

So,the art historian should be familiar with existing technical problems and threatening dangers,understand the physical structure and needs of objects in his field,be able to recognize symptoms of decay, know how to protect artifacts in display,storage and travel. He also has to know enough about methods of examination and research,and on the possible damaging influence of conservation treatment on the documentary features in objects. Last,but not least,he has to be prepared to organize rescue action in cases of catastrophes and emergency, and eventually to give "first aid" to objects when no conservator is available and it is a matter of "life or death" for the artifacts.

On the other hand, the art historian shouldn't carry personally any work of conservation, though he may know well what has to be done.He also will not be qualified enough to do technical scientific research even that he can know something on the particular kind of in-

vestigation. He shouldn't give authoritative opinions on technical matters in research works,publications,etc. without consulting a professional specialist in the relevant field.

The line of demarcation between what is correct and what isn't will depend,among other things,on the criticism,culture and common sense of the art historian.But there is one more requirement for the art historian's qualifications : he must have sensitive and understanding hands.Otherwise he is causing a lot of damage ,by breaking,tearing,crushing,creasing,or staining objects through carelessness or inexpert handling.This also is a very important point in technical lectures.Every conservator knows well this problem when he has to repair things damaged by persons taking care of objects.

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In conclusion of the considered problems the following can be said :

- it seems obvious that modern art history can not remain separated from certain specific matters connected with the physical substance in objects,

- conservators themselves are not able to ensure a proper protection of cultural heritage. They need the art historian as an ally.But he has to be well trained to give effective help,

- the matter as a whole has never as yet been considered from the practical point of view.There also are many different opinions on how this technical instruction for art historians should be organised. This very important and urgent matter is certainly in need of open discussion.

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CONCEPT AND TEACHING METHODS IN THE TRAINING OF RESTORERS AT THE DRESDEN VISUAL ARTS COLLEGE

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CONCEPT AND TEACHING METHODS IN THE TRAINING OF RESTORERS AT THE DRESDEN VISUAL ARTS COLLEGE

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The growing introduction of scientific working methods into the activities of restorers has led to a higher quality of the restorers' profession thereby calling for new and better training. The multitude of knowledge and capability, which a restorer must have in order to master more than merely manually individual processes, determine the training scheme. The mediation of all-round knowledge in technological, artistic, scientific and natural-scientific fields is an urgent necessity. The time when it was sufficient to learn for a few years from an experienced restorer or in a workshop, in order to be able to restore have long gone by.

Particularly in the course of the past twenty years numerous countries have, in consideration of this fact, established training centres of a school character.

It is interesting to note that the developed teaching concepts and views regarding the teaching methods differ everywhere, although all training centres aim at training highly-qualified restorers. The main problems might consist in answering the following questions:

- To what extent shoud restorers' training at a school bear basic character or be specialized

- The measure and kind of relation to practice

- What significance do we attribute to artistic, natural- and art-scientific training and which proportions are most suitable.

The character of restorers' training and the period of training should be determined by the demands made by the direction of the relevant specialization.

Anyone who nowadays intends to keep up with or take part in determining the international rate of development of preservation techniques for art treasures, must prepare the trainee in a rational and single-minded way, must set up institutions which are, as to apparatus, technology and personnel, capable of opening up processing and mediating information and knowledge. This means that the unity of theory, research and practice must be developed in an intensive manner.

In the following an attempt will be made to provide an insight into the instructional concepts and methods of restorers' training at the Dresden Visual Arts College. This takes place on the basis of the ten years' experience in training restorers at GDR colleges.

In the GDR there are two levels of training, the three-years' trade-school and the five years' college course. The latter nowadays exists only for the specialized disciplines of paintings and wood-sculpture restoration offering a total of 10 study places per year. In all other fields training takes place at trade-schools. The choice of an arts college as a place for training is based on the fact that the artistic stimulation, which a student of picture-restoring obtains at such a college, is indispensable for the development of his artistic capabilities. Likewise the handicraft and technological experiences of a restorer might be useful for a painter.

In Dresden an attempt has been made to find an effective structure which completely corresponds to the vocational aim of a restorer. The discipline of restoring, which at first is limited to training restorers of paintings, wood-sculptures and murals, is supplemented by the teaching fields of "basic artistic studies", "basic studies in natural sciences" as well as "scientific photography". For specialized training in the science of art and the preservation of monuments, special lecture programmes have been worked out. Likewise there is strong orientation towards the discipline of "writing" by mediating knowledge on the reproduction of historic writings. There are additional lectures on "plastic anatomy" and "perspective" which do not demand any special modification for restorers.

Instructional Methods and Concepts

The study-programme covers a training period of five years. The first year of study is, apart from the intensified theoretical training (social sciences, anatomy, perspective, language training), mostly reserved for basic artistic studies. We start with the idea that, before a student is made acquainted with the methods of preserving and restoring, he must have reached a certain level of his artistic capabilities for the restoring of paintings and sculptures. Therefore we will not desist from the fact that, apart from the proven immatriculation or leaving certificate, a successful examination of artistic skill is the basic prerequisite for admission to a study course.

From the 2nd to the 4th year of study, approximately 60 per cent of the specialized training is devoted to the teaching of restoration methods. Artistic training is continued up to the 4th year of study, and occupies roughly another 30 per cent of the study volume. The remaining 10 per cent of the specialized training are used for the mediation of relevant natural-scientific knowledge (chemistry, physics) and the learning of the most important photographic processes in various fields of radiation for the examining of works of art and the documentation of the restoration measures.

During the final year every student is assigned a major restoring project which he must carry out independently. He is supposed to supply evidence of the knowledge he has acquired and his capability of applying in practice. A pictorial job and the tackling of a smaller research theme are also part and parcel of the diplomatheses.

The essential principle of specialized training for all fields of instruction consists in the mediation of knowledge, particularly related to practice. No series of theoretical lectures takes place without practical exercises. The students learn the various working methods, ranging from the examination of the object and documentation photography to preserving and restoring immediately a suitable piece of art. We hold the view that, from the very first day of training, every student must become aware of a high degree of responsibility towards the works of art he is supposed to look after. Each student is given between 3 to 5 objects (according to size and degree of difficulty) which he examines, documents, preserves and restores during his training period. Weeks of practice are provided for operations which have not been completed during lectures. Thereby every student is able to follow the course of work on "his" object. Moreover annual summer practices, lasting between 3 and 4 weeks, are organized outside the college.

Thereby the college, at the same time, fulfils an important social commitment. In the course of the years it will be possible to restore a multitude of paintings and sculptures which are of minor artistic value but never-the_less deserve to be preserved as historic, cultural documents and to re-utilize them for the equipping of historical rooms in palaces and museums.

In order to safeguard a certain methodic breadth of the restoring processes, in every year the training objects are selected in such a way that each student has the opportunity to become acquainted with additional variants through contact with objects of his fellow-students, apart from processes practiced by himself. The training

programme is structured in such a way that the students, beginning with the documentation and examination of the object up to its completion, become acquainted with all the operations in a logical sequence. The subject distribution plans of all the fields of instruction are precisely coordinated and structured so that the students are provided, in accordance with the practical exercises, with the relevant theoretical knowledge.

Well-founded training in the sciences of arts and society is of major importance for the budding restorer. Just as the training in the arts and natural science is completely directed at the professional aim and modified correspondingly, lectures on the science of the arts and society cannot be limited to the mediation of general knowledge. The established curriculum for specialized art history is concentrated upon the period of the preliminary stage of the Romanesque style up to the 19th century. The future restorer must be able to know, evaluate and integrate the art treasures of his future field of work. He must be familiar with the major methods of art historic research. Specialized knowledge in the field of arts and natural science are indispensable for the restorer's subsequent qualified cooperation in research assignments.

It is just as important that, apart from general sociological education, specialized lectures and seminars deal with problems of the relationship to the cultural heritage and the inclusion of the historic work of art into the social process of our epoch. To meet his future tasks he needs more than a high restoring skill.

The students are, to a growing extent, made familiar with the research themes and included by means of partial tasks carried out during their training time. We regard it as a vital issue that they are made acquainted with methods of research work and intellectual processes directed at solving a problem.

Only in this way will it be possible for the students to solve, within their diplomatheses, minor research problems and to work out correct questions. Their cooperation with natural and art scientists must seem a matter of course to the students after five years of studying.

Recognition and Promotion of Talents

We are aware that even a five-years' college study course can mediate merely basic knowledge. We are therefore increasingly endeavouring to set up a system of preparing interested applicants for the study course and the de-

velopment of criteria for the selection of the most suitable applicants. The latest endeavours in the whole of the GDR to construct a system devised to recognize at an early stage and to promote talents in the field of visual arts will also benefit the training of restorers by means of the higher quality of the applicants. All pupils of the 9th grade who show talent in the field of visual arts are allowed to participate in a "preliminary aptitude examination" in the various counties, which take place once every year. Experienced teachers from the art-schools and colleges select the most talented pupils and organize their systematic artistic advanced education by way of evening classes.

By dint of the increasing setting-up of practical trainee positions for restorers within the Institute for the Preservation of Monuments and several museums, nearly all applicants will in future be able to gather practical experience prior to beginning their studies. Now as before it is recommended to learn a handicraft prior to studying. Special importance is allotted particularly to the development of craftsmanship if the restoring of paintings on wooden boards, wood-carvings, murals or arts and crafts is to take place. Particularly suitable for this are trades such as carpenter, cabinetmaker, painter and decorator, gilder, art-metal worker etc.

More attention than hitherto will also have to be paid in future to the advanced training of restorers following the awarding of the diploma or after leaving a trade school. Increasing obligations might, in this context, be laid at the door of the training centres.

SUMMARY

The growing introduction of scientific working methods into the activities of restorers has led to a higher quality of the restorers' profession thereby calling for new and better training. In the GDR there are two levels of training, the three-years' trade school and the five years' college course. At the Dresden Visual Arts College an attempt has been made to find an effective structure which completely corresponds to the vocational aim of a restorer. The discipline of restoring, which at first is limited to training restorers of paintings, wood-sculptures and murals, is supplimented by the teaching fields of "basic artistic studies", "basic studies in natural sciences" as well as "scientific photography".
The study-programme covers a training period of five years. The essential principle of specialized training for all fields of instruction consists in the mediation of practice-related knowledge. Special attention should be paid to the selection and preparing of the most suitable applicants.

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LES BASES DE PRINCIPE ET DE PRATIQUE DE LA FORMATION DES RESTAURATEURS EN HONGRIE

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LES BASES DE PRINCIPE ET DE PRATIQUE DE LA FORMATION DES RESTAURATEURS EN HONGRIE

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L'artiste, comme l'un des représentants caractéristique et particulièrement apprécié de la capacité créatrice humaine, est depuis des millénaires un personnage connu et reconnu par la culture. A l'opposé de lui le restaurateur a une profession beaucoup plus jeune, on pourra dire toute neuve, qui est un branche latérale de l'artiste, et dont la nature indépendante se consolidait que dans les derniers temps. L'artiste et le restaurateur s'enchaînent organiquement, l'objet de leur activité: l'oeuvre d'art est analogue, mais chacun y approche d'une autre côté. Cette parenté et à la fois différence est devenue graduellement consciente, et c'est exactement la formation des restaurateurs, qui y fait jaillir unanimement la lumière. L'exigence et la nécessité de la formation n'est pas une qualité émergent subitement, mais la conséquence logique d'un longue procès, dont la réalisation dépend de beaucoup de prémisses. Ainsi l'évolution historique, que nous pouvons saisir, n'est pas seulement intéressant en soi-même et en son développement, mais en même temps détermine et définie ces aspects décisifs aussi, qui forment la base de la programme, l'objectif et l'atmosphère de la restauration. Ainsi la revue concise des prémisses historique de la formation des restaurateurs peut donner une réponse et une justification sur le développement de cette opération culturelle devenant dans nos temps plus et plus importante ainsi que sur son état présent, et peut assigner ces directions principaux vers lesquelles elle sera capable de s'acheminer dans la future. Avant cette époque l'exigence ne s'est jamais prononcée, qu'on doit préserver une création humaine simplement parce qu'elle est vieille. La production de l'art a parlé à son propre époque, ainsi dans sa forme, son contenu, que dans sa destination. Le changement de ces qualités a résulté dans la modification, la transformation, de même la destruction du bâtiment, de la statue, de la peinture et d'autres objets d'art, et a provoqué leurs remplacement avec des objets nouveaux, répondant à les exigences du nouvel époque, à son goût. C'était seulement à la rencontre du 18-ième et 19-ième siècle - dans l'état d'esprit enthousiaste des grandes fouilles archéologiques commençant à Pompei, - devenu évident que l'estime des oeuvres du passé a une force obligatoire. La romantique s'est tournée vers les valeurs nationaux révolues, el a cité les témoins "de la gloire ancienne". L'ancienne comprend en soi la notion de l'originaire, qui est digne d'être connue, de conserver et pour servir comme example pour

les générations futures. L'honneur de l'ancienne est considérablement agrandie envers le nouveau. C'est ainsi que l'exigence pour la conservation des oeuvres du passé se cristallise, qui se dirigait au commencement seulement à l'état premier, et plus tard déjà à tout le processus vital de l'oeuvre d'art. Cette dernière manière à voir du 20-ième siècle a développée les aspirations pour la plus grande authenticité possible, ainsi historique, que matériel. En sense historique de façon que l'opération de la restauration en quelque forme prends en observation chaque état historique de l'oeuvre, et en sense matériel de façon de l'originalité pas seulement en esprit, en forme et en structure, mais aussi dans la consistance visible et invisible du matériel de l'objet d'art. Le 19-ième siècle n'a souligné que les valeurs nationaux, tant que notre époque tient toutes les sortes des oeuvres d'art des nations particulières pour la valeur de toute l'humanité, et ainsi leurs conservations devient pas seulement un devoir nationale, mais aussi humain.

Ils s'associent beaucoup de point de vue pratique et important aussi à les prémisses de principe, expliquer courtement, de la restauration, et ainsi de la formation des restaurateurs, dont une partie a un caractère matériel, respectivement technique. L'assurance des matériaux et utensils nécessaires parait au premier instant si naturel, qu'il est dommage le mentionner du tout. Mais ce n'est ainsi qu'en apparance, en effet les procédés technologiques se développent de plus en plus vite, et ainsi les matériaux, comme les moyens de travail nécessitent un développement progressif permanent. L'histoire de la restauration est en cet égard la longue série des expériences, qui se continue en conséquence des devoirs augmentants. Comme chaque cas est plus ou moins individuel, les concernants procès sont de même individuaux, ainsi il est nécessaire une amélioration permanente en matériaux et en utensils aussi, et l'ouverture de nouveaux fuites. L'exigence en principe d'originalité du matériel de l'objet d'art étaye encore de plus la demande en question.

L'application du matériel, de l'utensil, du procès technologique nécessite l'existence de dispositions manuelles du restaurateur, un haut degré de savoir et culture en artisanat, une routine professionnelle assurée, la capacité de réaliser les techniques des plus différents âges de l'histoire précisément et délicatement, en pratique.

Mais la pratique a aussi une côté spirituelle et de tenue, qui ne peut être pousser à l'arrière-plan à côté de la partie technique. Comme il s'agit de la restauration des oeuvres artistiques, le restaurateur doit aussi être un artiste, avec un savoir artistique en pratique.

Mais sa position de départ en face de l'objet d'art est différent de celle de l'artiste créatif. C'est que la restauration n'exige pas une force créatrice active, mais une capacité reproductive d'un très haut niveau, laquelle est capable d'avoir l'intuition de l'évolution millénaire de l'art et peut s'exprimer avec savoir artistique toujours humblement en l'objet d'art, lequel de tous temps entre dans ses mains. L'individualité du restaurateur s'exprime dans cette attitude. Mais il est nécessaire qu'encore une disposition, de plus conviction s'associe, c'est-à-dire, que le sens et le but primaire de sa fonction doit être l'assurance de la vie suivante de l'oeuvre d'art. Il ne travaille pas pour lui même, mais pour les objets d'art immortels. Pour cela tout ses procédés, même en cas de non-réussite, sont affaires publiques. Son travail est plus ou moins une intervention dans la situation présente, dans le destin future de l'objet d'art, et ce n'est pas indifférent ni de la point de vue du présent, ni des avenir. Ainsi il doit reconnaître l'obligation professionelle et morale de la documentation. Pas seulement pour cela que son activité doit être appréciable en nos jours aussi en détail, mais pour cela aussi qu'il produit une base sur pour les restaurations suivantes. On doit supprimer les secrets de la guilde, qui a malheureusement vécu le plus longtemps au territoire de la restauration. La formation des restaurateurs n'est point imaginable sans cela.

L'ouverture de la practice de la restauration est encore nécessaire dans d'autre sens aussi. Le progrès technique et scientifique s'agrandi immensement sure depuis le siècle passe, et la restauration doit marcher au pas. Les sciences de la nature et la sociologie et les solutions techniques

ouvrent de plus en plus large perspectives ainsi sur le territoire du savoir propre, que du savoir générale humain. Le restaurateur et encore plutôt la formation des restaurateurs doit reconnaître et utiliser pour la solution moderne de ses propres devoirs des possibilités d'approche les plus variées, veillant sur l'état d'équilibre des innovations et de la pratique. Cette attitude de la pratique est de plus importante, parce que l'exigence de la restauration s'étend de nos jours sur toutes sortes d'oeuvres. Cette activité est restée au commencement et encore longtemps à la domaine de la peinture. Aujour'dhui il n'y a plus de limite de genre, de l'époque, ni de branche d'art et la tâche est devenue immensement plus grande ainsi en quantité, comme en qualité. La valeur nationale de l'objet d'art s'est élargie à valeur humaine, qui vient d'être accompagné de l'exigence de la collaboration mondiale. Seulement la réalisation de cela peut donner une possibilité pour essayer de donner la solution à des tâches devenues gigantesques.

A la base d'esquisse courte et la caractéristique des prémisses en principe et pratiques il s'impose à la formation hongroise des restaurateurs une voie ternaire: la voie de l'art, de la technique et de la science. Ça veut dire trois facultés, mais pas séparé l'un de l'autre, mais en collaboration. Le sens et savoir artistique, la disposition manuelle et technique, les connaissances de l'histoire de l'art et de la civilisation et les investigations de sciences de la nature concernant ces problèmes: donnent les éléments, dont la voie ternaire se compose. Chaque branche d'études a ses spécialistes, ainsi le restaurateur n'est ni physicien, ni chimiste, ni historien d'art, mais le médecin de l'objet d'art. Mais ces spécialistes travaillent ensemble pour servir le but. Il est nécessaire pour y arriver, qu'on trouve sur la territoire de plus en plus compliquée de la restauration, la langue commune. Qu'on puisse poser des questions l'un à l'autre et mettre à profit les réponses sur leurs propres domaines. Au centre de cette opération collective on ne trouve pas l'activité ellement, mais l'objet d'art avec sa propre individualité matérielle, esthétique et historique, avec son influence social interpreté la plus largement. Les pertes graves des oeuvres artistiques hongroise, vis-à-vis des autres pays européennes, à cause de l'évolution historique disgracieuse, et l'état défavorable de relativement petit nombre des oeuvres existantes motivent au même degré et font spécialement important la prédominance décisive de la position de l'esprit développer en haut. Dans l'évolution de la formation hongroise des restaurateurs les phases historiques esquissées et l'harmonie des exigences culturelles de chaque fois étant en relations avec elles, a joué un rôle dirigeante. Dans l'intérêt pour réaliser les perspectives suivantes il est indispensable de s'encadrer activement dans la collaboration internationale et de développer continuellement et avec intention les connexions établies.

78/22/5

PRESERVATION OF AFRICAN CULTURAL HERITAGE: WHERE ARE THE TECHNICIANS?

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PRESERVATION OF AFRICAN CULTURAL HERITAGE: WHERE ARE THE TECHNICIANS?

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ABSTRACT:

In preparing this short paper, much attention has been paid to the problems facing Africa as a continent, especially Africa South of Sahara, in obtaining the technicians for the preservation of her cultural heritage. This problem had to be tackled from training points of view because of the nature of museum profession. Once the problem of obtaining trained technicians is solved, other problems, which are secondary will be easier to tackle. The major cause of inadequate number of trained technicians are enumerated and possible remedy suggested as well as areas where the ICOM Committee for conservation could be of assistance. The technicians needed for the smooth running of the African Museums (excluding Administrative Staffs) are the field technicians; conservation and exhibition technicians. Other areas of co-operation are those of availability of either institutional trainings or "missionary" type of training. Finally, possibility of research and reduced constraints in obtaining all the tools and equipments from overseas.

At conferences, assemblies and seminars, one of the cardinal points always discussed is the question of how to

have enough technicians for museums. It is regretable that conservators and museum specialists were not taken seriously enough despite the fact that it is on them depend the survival of our heritage. Much as progress has been made in this field, this progress is yet inadequate and in the case of Africa, insignificant. The African situation is acute for three reasons:

(i) lack of enough training facilities within the continent and;

(ii) inavailability of the type of equipments with which the few Africans trained outside the continent have been trained with;

(iii) inadequacy of fund at the disposal of museums so as to establish research laboratory where research could be carried out on local materials.

Broadly speaking, the museum technicians are made up of three groups:

(a) the field technicians;

(b) the conservators or restorers and

(c) the exhibition technicians.

If it is accepted that the areas of conservation training should include collection, examination, care and management, restoration and conservation treatment; as well as exhibition conservation, one will then see why the three groups of technicians mentioned are related. Both the functions and activities of the three groups are so interwoven that, if it has been possible it may be ideal that the same person performs all the three functions.

But what is ideal may not be practicable and this is the case in Africa.

The field technicians:

The training of this group of technicians are more of psychological approach to their tasks than technical. When one realises that majority of the people possessing the authentic objects are illiterates and live more in villages than cities, one then appreciates the task before these group of technicians. Furthermore, the owners attach very great importance to these objects to the extent of their refusal to part with them. To this psychological training are the facts, that for a trainee to succeed, he/she must be able to speak the dialect of the area and in addition, must integrate himself with the community before he is ever listened to.

The latter condition scares away so many potential technicians under the present situation of villages in Africa. Those who are able to support the first stage as stated above, then come to the final stage, which is the one of training on how to document the objects.

Training in Documentation, in majority of cases, is by learning on the job. This has been effective in some of the old museums, where people with long experience could disseminate their knowledge to the younger ones. Since their is practically no institutional training facility for such course, the hope for the future is by bilateral assistance between African Countries. Though assistance may be sought outside the continent,

but to what extent such assistance will help in minimising the task, could not be easily estimated. In order to combat this problem, the probable approach will be training on the jobs within the continent, though the experts may not necessarily be from Africa. Seminars, lasting for few weeks on particular topic related to field collection, where museums technicians within the region could attend, will be the immediate approach. I refer to regions rather than countries, in that, in general, objects within the same region are similar, though may be called different names.

The field technicians having succeeded in acquiring the objects and bringing them to the museum, the great task of preserving these objects for the present and future generations, then falls on the next group of technicians who are called conservators/restorers. Though formation of the field technician is a task, that of the conservators, is a greater one, especially when one realises that an error made may be irrepairable. As stated by Dr. N. Stolow, the formation of conservators/restorers are in different categories. These categories include professionals, practical conservators in a variety of disciplines and conservator technicians. The professionals are the chemists, physicists and biologists engaged by museums so that their investigations and researches have practical meanings to the problems at hand.

Means of preserving objects and allowing for their use as educational and cultural tools requires careful collaboration and co-operation between conservators, curators and exhibition organisers since the process of conserving an

object or collection is the product of a partnership between appropriate training designed to enable them communicate. While the Curator is primarily concerned with the historical and aesthetic aspects of an object in his collection, this is less appreciated by some conservators especially since these are issues that a conservator will receive very limited training. In order to bring both the conservators and curators closer in order to communicate meanifully, the curatorial staff, particularly long-established and senior members, should receive in-service training in conservation theory and practice.

Conservation in any museum context refers to the technical and scientific activities associated with the examination, restoration treatment and on-going care of collection so as to preserve them for future generations. One cannot arrive at treating or preserving an object without the basic understanding of how the artifacts and objects are put together. The first laboratory for this purpose in United States of America was built in 1925. If today United States of America still have shortage of conservators, one will then appreciate while Africa is in desperate need of these professionals. Evidence of this inadequate production of trained conservators and technicians is in the repeated mention of conservation training in recommendations and resolutions at International Congresses of ICOM and UNESCO.

Conservation, though, a discipline like any other arm of museum services, it is more delicate a service. This then

shows why it is a service where an untrained person should never be assigned to work. While an error in documentation or photographing of an object could be rectified at a later date, an error in the treatment of an object will falsify the object and deforms its authenticity for life. Since the practice of conservation in Africa is geared to the collection needs, then the training programme must be designed to meet such needs and to anticipate future requirements.

Accepting that the main objectives in the training of conservators are:

(1) to provide an academic background to allow the conservator not only to do his own studio/laboratory work but also to advice on and supervise matters beyond his station.

(2) to allow the development of those skills vital in the conservator's chosen field.

(3) to ensure the highest possible standards of attainment in (1) and (2) above.

Training facilities could then be classified within these major categories:

(a) Museum/Studio Exposure

(b) In-training

(c) Training of the "Missionary" type

(d) Regional Centre Systems

(e) Institute Training

(f) University training.

The first problem is that of availability of training

institutions. This is a world-wide problem. In the case of conservation, the problem becomes more acute. This is due to the fact that not only getting attachment training in museums is difficult, but majority of museums have not got the facilities for training in conservation. And when one thinks of established institution adequately equiped for such training, one can count them at one's finger tips. There is non in Africa specially established for this objective. I know the question I will be asked is what of Jos Centre? My answer is that Jos Centre cannot fulfill this purpose because conservation is just one of the eight courses being taught, within one academic session, in Jos.

When one considers that there are few museums that can boast of trained conservators in Africa, one will then agree that for someone to be trained as a conservator, in order to be able to work on his own, it will take a minimum of eight months. Only after such a period can one feel that he can manage on his own without the supervision of more experienced person, in the same field, in his museum. Since the museums outside Africa are not able to meet the demand for training within their own region, the chances of meeting the full demand from other regions is very meagre. There is plan to organise training of conservators in the five regional centres (in different parts of the world) so that at least the trainee could be sure of obtaining full training for at least eight months.

The conservation problem varies from region to region and as such I am of the opinion that one gains more by

learning in one's region. When one studies in a region different from his, one is bound to re-adapt what he has learnt, in order to meet the problem of his region. And, I am sure it is not with basic training of two months that one will be able to overcome this.

There is also the problem of the choice of right calibre of people for this course. In majority of cases, on observes that majority of the museum staff are without the basic background of pure sciences (i.e. physics, chemistry, biology) not to say graduates in pure sciences. If problem of shortage of conservation technicians/conservators is to be reduced, then museum authorities should start encouraging people with science background to come into the field. Training of such people, be it in the junior, intermediate or senior cadres, will be easier and more rapid than training some-one who has never learnt, not to say work in a laboratory of chemistry or physics in his life.

Establishing a conservation laboratory requires a lot of fund and this is a problem especially taking into consideration the meagre financial resources of museums in Africa. Nothing is more frustrating than being trained in one job and not having the possibilities of practising that job in which one is trained. In the light of this problem it would be advisable that there should be more collaboration between African museums so that museums where facilities for conservation is available should extend their services to those who have not.

As an interim solution to the acute shortage of staff in this field, it may be necessary to access the facilities available in the few museums that have got conservation laboratories/workshops. Knowing fully that it is only three major materials that form over eighty per-cent (80%) of both ethnographic and archaeological materials in Africa, it may then be possible to organise training in the conservation of these three major materials. These materials are:

(1) Wood;

(2) Stone and pottery;

(3) Metals (copperalloys and iron).

If for example, the laboratory in A country is better equiped for wood conservation, training in wood conservation for a period of three months could be organised for trainees from all member states. If laboratory in B country is better equiped for metal, training in metals for three months could be organised there and same thing for country C which may be better equiped for stone and pottery treatment. Under such arrangement, within nine months and within the continent, it will be possible to overcome, to a certain extent the shortage of staff in this field. This will then supplement the few staff that are able to be trained in other parts of the world.

Three years ago, in Venice, Italy, an appeal was jointly made on behalf of the third world by delegates from Nigeria, Japan and India as regards ways of solving obstacles as far as equipments and chemicals are concerned. As for Africa, this problem is yet unsolved. If I have to mention this,

it is because the few trained technicians find it difficult to work with the type of equipment they had their training in Europe or America. I need not repeat the major constraints as these are well known to majority of delegates. Since, the possibilities of having research laboratories in Africa in the immediate future is not sure, one assistance this assembly will be rendering to Africa, is by assisting her in conducting research into some of her local materials which are been used for conserving the cultural objects. This could be done in collaboration with some of the few trained conservators from Africa. And through the "Missionary" type of training, results and applications of such research can easily get to all institutions dealing with preservation of cultural heritage in Africa.

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78/22/6

THE TRAINING OF RESTORERS FROM THE MUSEUMS OF THE RSFSR IN THE RUSSIAN ART RESTORATION CENTRE I.E. GRABAR

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THE TRAINING OF RESTORERS FROM THE MUSEUMS OF THE RSFSR IN THE RUSSIAN ART RESTORATION CENTRE I.E. GRABAR

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The young restores - graduates from the high and secondary art schools - do receive professional and general education, but naturally enough their practical experience in the specific field of restoration is limited. It is well-known that in the restoration of the works of art the lack of experience couldn't be compensated by the theoretical knowledge and the experience can be attained only with years.

That's why a young specialist sent by the institute to the remote museum, where there is no experienced teacher, is bound to limit his activity to some relatively simple operations. It happens that the management of the outlying museum invites to the vacancy of restorer a young painter or an art critic with no professional preparation at all. Young specialist of this kind is not permitted to perform any restoration or conservation work, until he acquires necessary knowledge and professional skills.

And here comes to help with its training courses one of the biggest restoration institutions of the USSR. The training of restores from the museums of the Russian Federation usually has place in the All-Russian Scientific Art Restoration Centre I.E.Grabar.

The training is systematic. Every young restorer comes to study regularly once or twice a year for several years. Usually the duration of every training term is 30 days. In these 30 days a young specialist receives necessary additional knowledge and assimilates the technique of one of the restoration operations or more complicated versions of the known methods.

The first aim of the training is acquiring of indispensable volume of knowledge and broad practical experience in order to receive the state certification of the higher degree of professional qualification.

The Russian Art Restoration Centre I.E.Grabar exercises control of the conservation and restoration of the works of art in the museums of the RSFSR. In this connection the Russian Art Restoration Centre not only teaches the museum specialists but supervises their work in the museums and organises their preparation for the successive certification.

The training of the museum workers is being held in two ways: 1) courses of improvement of young specialists' qualification and 2) individual training. The first system is the most opportune for the preparation of young specialists for the first certification. It is possible to carry on the group lessons when a teacher has five students in the same time. Besides the study process includes lectures or even a number of lectures on the subject that is necessary to know at this stage of training.

The individual training is more preferable for improvement of professional qualification of restores who have already some experience. It gives the possibility to esteem individual capacities of a student and the peculiarities of the museum collection in his charge.

It is worth to mention that for the practical lessons we use as a rule the works of art from the same museum where the student works.

This principle helps to solve a number of practical tasks. First, it allows to teach a student in correspondence to the concrete needs of the museum collection in his charge, considering the peculiarities of the collection and the state of conservation of objects. Second, a restorer can observe for a long time the state of the work of art, restored by him, controlling in this way the results. And finally at the higher stage of the training this system allows to give a student "a home-work". In this case a part of restoration work is done during the training and the other part - independently in the museum after the pattern. During the next term of training a student has to render an account of the work fulfilled independently, demostrating photos, illustrative documents and if neccesary a restored object itself for the estimation of his work.

The independent fulfillment of the part of the training work helps to make the most of the training time and to speed up the professional level of a restorer.

It is obvious, that collections of various museums are very different in their composition. This requires considerable differentiation of the training programmes. For example, the museum that has a collection with the prevalence of oil-painting or medieval icon-painting is interested in the particular specialization of its restorer, even if he is the only one in tha museum. On the other hand, the museum with relatively small collection of different exhibits can prefer a restorer who is able to render first assistance to all the heterogeneous objects of the collection and who can make all the necessary preparative works for the exhibition of the objects.

In this case the training could consist in gradual study of simple operations of conservation and restoration on the works of art made of different materials and in different techniques.

Having obtained the first certification in one of the specialities, a restorer of such a museum begins to study another speciality which is necessary for the museum. In such way a restorer soon becomes a kind of "universal" specialist, but he has to "pay" for it with a slow growth in the skill.

This system may be useful in the case when a restorer has in his charge a small collection of different works of art. In big museums it is preferable to have two or more highly qualified restorers.

The training of restorers is carried on according

to annual and perspective plans of the Centre; the necessities of museum and their requests are taken into consideration too.

Plans of individual training of students are elaborated by respective teachers and approved by the Restoration Council of the corresponding department. The Restoration Council supervises the process of study and when it is over estimates the fulfilled work, professional knowledge and experience of the students.

The Resotration Council consists of the most qualified specialists of the Russian Art Restoration Centre. Specialists of adjoining professions are often invited for resolving different practical needs.

The training in the Centre is gratis.

Personal expences of students connected with travelling to Moscow, hotel accomodations etc. are paid by the museum where the restorer is engaged.

78/22/7

ENSEIGNEMENT DE LA CONSERVATION
ET MATERIEL DIDACTIQUE

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ENSEIGNEMENT DE LA CONSERVATION ET MATERIEL DIDACTIQUE

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ABSTRACT

Le niveau des travaux effectués en conservation et en restauration peut être élevé en formant les conservateurs et en établissant des écoles de restauration. Mais les méthodes d'enseignement n'ont pas beaucoup changé. Aucun matériel didactique n'a été fait et les connaissances ne peuvent s'acquérir qu'au contact direct des enseignants. Les livres, les films, les diapositives, les fiches techniques produisent des impacts très différents sur les élèves et les stagiaires.

Durant les dix dernières années de nombreux cours pour restaurateurs ont été créés. Organisés par des instituts internationaux et nationaux, des universités ou des privés, ces cours répondent à un besoin évident: le patrimoine, pour de nombreuses raisons qui ne seront pas étudiées ici, se détériore soudain beaucoup plus rapidement et, de tous cotés, on s'efforce d'éviter des désastres par des travaux de restauration qui demandent des spécialistes.

Ces nouveaux cours sont-ils la réponse aux problèmes posés ? La réponse est malheureusement non car ce n'est pas en formant quelques restaurateurs par an que l'on pourra sauver le patrimoine qui nous a été légué par les générations précédentes. Il faudrait que parallèlement aux cours pour restaurateurs, soient organisés des cours pour administrateurs, responsables des collections, historiens d'art et scientifiques, qui, par leur pouvoir de décision, ont en leurs mains la solution aux problèmes de conservation des collections entières. Il est à regretter qu'un effort ne soit pas fait dans cette direction. Quelques soient cependant les personnes à qui vont s'adresser les cours de conservation et de restauration, il est très intéressant d'étudier les problèmes qui se posent à celui qui décide d'organiser un cours. Si les problèmes financiers sont résolus le responsable se trouvera devant 3 questions:

- Quel sera le programme ?
- Quels seront les enseignants ?
- Quel sera le matériel d'enseignement ?

Programme

Il est très étonnant de constater que certaines personnes estiment que la restauration ne s'enseigne pas. Elle fait partie de ces domaines artistiques où les dons et la main priment tout, l'expérience faisant le reste. Cette façon de présenter le restaurateur est très dangereuse et conduit à des catastrophes. Le restaurateur face à l'objet est un peu comme le chirurgien face au patient. Certes, le don, la main et l'expérience sont très importants pour le chirurgien mais, avant d'opérer, il a dû suivre sept années de médecine générale où il aura appris entre autres, l'anatomie et les symptomes des maladies.

Il en est de même en restauration où de très nombreuses connaissances théoriques sont absolument essentielles à un bon restaurateur. Celles-ci peuvent et doivent être données par un enseignement systématique progressif, qui devra passer par les 5 étapes suivantes:

- structure de la matière
- technologie de l'objet
- causes de détérioration de l'objet
- conservation de l'objet
- restauration de l'objet

Tout enseignement qui, pour des raisons diverses (manque de personnel, manque de temps, etc...) chercherait à sauter une ou plusieurs de ces étapes n'aboutirait qu'à de mauvais résultats.

Enseignants

Le programme étant défini, il faut maintenant trouver les professeurs et assistants. Ceci est une gageure car peu de spécialistes se sont intéressés à la structure, technologie et détérioration des objets sous l'angle de vue de l'oeuvre d'art et en ce qui concerne la conservation et restauration les nombreux restaurateurs qui ont de l'expérience pratique ont en général peu d'expérience d'enseignement et peu de don pédagogique. Il a souvent été dit en effet que de par son mode de travail en contact direct et intime avec l'objet, le restaurateur trouve de grandes difficultés à exprimer son expérience devant un groupe d'élèves.

Ceci étant posé, il devient clair que les enseignants vont être rares, vont être disputés entre différents centres de formation et que le contact capital qu'ils pourraient avoir avec les élèves qu'ils forment sera extrêmement bref. D'où la nécessité de transmettre leur expérience au moyen de matériel didactique qui restera lorsque l'enseignant sera parti.

Matériel d'enseignement

Nous arrivons là à un point essentiel et qui, malheureusement a été peu étudié, ce qui, peut-on penser, a fait stagner le niveau des restaurations depuis un certain temps. Il est intéressant de constater que, si dans le domaine de la conservation et de la restauration les publications sont assez nombreuses, beaucoup sont hautement spécialisées et ne s'adressent qu'à un public déjà formé, certaines sont une source de recettes à ne remettre qu'avec précaution dans des mains même expérimentées, quelques unes sont totalement inutiles, d'autres enfin et elles sont rares sont assez générales pour donner un leger aperçu des problèmes posés par le métier.

Qui n'a pas eu à répondre à la question suivante posée par un jeune voulant débuter : "Quel livre dois-je lire ?"

Si le choix dans des livres est très limité, il est absolument nul dans les autres types de matériel d'enseignement. Dans d'autres disciplines, du travail a été fait pour mettre au point du matériel didactique qui va du livre au film, en passant par les diapositives, le modèle, la vidéo-cassette, la fiche, etc. Dans l'enseignement de la restauration rien de tout cela et on reste,à part quelques exceptions, dans le domaine de l'improvisation.

Chaque type de matériel ayant un impact très différent suivant les disciplines, il semble intéressant d'étudier l'impact que le livre, le film et les vidéo-cassettes, les diapositives, les fiches auront sur un restaurateur.

Il est à noter avant de commencer cette étude que la conservation et la restauration s'appliquant à des objets, l'élément visuel du matériel sera d'une importance considérable(au moins autant que dans l'enseignement de la médecine). La proportion illustration-texte devrait être grande, ce qui entrainera un matériel particulièrement coûteux.

Le livre: Il apporte des données mais ces données souvent évoluent vite dans une profession qui se cherche. Pour des raisons économiques, le livre est peu illustré et rarement en couleur. Comme les auteurs désirent faire le tour de la question ils mettent très longtemps à écrire, à recueillir et à contrôler leurs informations et comme ils ont par ailleurs des occupations très prenantes, le livre ne voit le jour que longtemps après sa conception. En resumé, le livre coûte cher, n'est pas toujours à la page, et est trop peu illustré.

Le film: 32mm 16mm: S'il est bien produit, il coûte très cher et les auteurs seront tentés de l'amortir. Le public des musées étant limité les auteurs chercheront à le diffuser auprès du grand public (télévision, cinéma). Changeant de public, les auteurs risquent de faire de la vulgarisation et les buts didactiques précis disparaissent. De plus ces films demandent des appareils de projection et des salles qui ne sont pas toujours à la portée des centres d'enseignement.

Le film 8mm et super 8: Plus facile à projeter, ces films perdent beaucoup en qualité. Ils aident beaucoup s'il faut illustrer la dynamique d'une opération. Cependant pour atteindre pleinement leur objectif, le but de ces films doit être bien précis dès le départ, le scénario bien monté et les opérations doivent être faites exprès pour la prise de vue. Des textes, panneaux explicatifs, diagrammes doivent être inclus dans le film. Malgré toutes ces précautions, le film passant rapidement, il est difficile parfois pour un élève de saisir un passage et de faire un retour en arrière. De plus, ce type de film n'est que rarement accompagné d'une bande sonore. Pour toutes ces raisons, il ne peut être utilisé que pour décrire des opérations très particulières et ne devrait pas durer plus de 5 minutes.

La vidéo-cassette: Système très intéressant pour un enseignant qui a été parfaitement mis au point. Le réalisation d'une cassette demande un travail énorme de préparation et une technique de tournage employant 2 caméras pour rendre l'action plus vivante. Le temps employé par l'enseignant à préparer la cassette sera largement recupéré puisque le cours pourra alors être largement diffusé. Les passages importants ou mal compris pourront être aussi facilement revus. Par contre, l'appareillage n'est pas encore standardisé, il coûte très cher et le contact enseignant-élève est perdu.

La diapositive: Elément le plus employé dans l'enseignement actuel, elle ne peut dans la plupart des cas être utilisée que par celui qui a pris ou fait prendre la photo. En effet, si en histoire de l'art, la photo d'un tableau célèbre pourra être utilisée par quiconque, la photo d'une étape de restauration d'un objet - détachée de son contexte - ne peut être commenté que par celui ou ceux qui ont collaboré au travail.

Par ailleurs la documentation photographique d'un travail peut être faite dans des buts très différents. La documentation photographique en vue de l'enseignement est très spéciale, bien plus complète, ce qui entraine la plupart du temps la présence et les directives du futur utilisateur au moment de la prise de vue. Malheureusement trop souvent les restaurateurs ne sont pas les

photographes et sont trop absorbés par leur travail pour s'en détacher un moment pour documenter une phase importante. N'étant pas orientés vers l'enseignement, ils ne connaissent que "l'avant restauration" et "l'après restauration" ce qui limite notablement les possibilités d'utilisation pour l'enseignement de documentation de travaux importants qui furent faits dans le passé. En fait, il faudrait arriver à exécuter des travaux spécifiques dans le seul but d'en documenter chaque phase.

Enfin la diapositive isolée est aussi peu explicative qu'une page qui a été arrachée à un livre.

Si l'on veut donc pouvoir utiliser la diapositive largement pour l'enseignement et la diffusion, cela devra être fait au moyen de séries accompagnées d'un texte écrit ou enregistré sur bande magnétique.

La fiche: Les fiches illustrées de photos sont des éléments de référence très utiles en conservation et restauration. Se limitant à un sujet elles devraient être illustrées très généreusement par des graphiques et des photos qui seront expliqués d'une manière aussi concise que possible. Lorsque l'information est dépassée, la (ou les) fiches pourraient être remplacées et, si l'index est bien fait, les nouvelles fiches pourront être ajoutées. Les illustrations devraient correspondre évidemment aux diapositives projetées durant les cours ce qui augmente l'impact et donne la possibilité aux élèves de venir vérifier les passages qu'il a mal saisis. Par ailleurs, les fiches essentielles peuvent être photocopiées ce qui permettra non seulement de diffuser les dernières informations auprès des personnes extérieures mais encore de donner aux élèves à la fin du cours ou du stage un résumé écrit des notions qu'il a dû acquérir.

L'enseignement de la restauration s'est transformé au cours de ces 20 dernières années. Le rapport 1 maître 1 élève est passé à 1 professeur 5/10/15 élèves. Les méthodes d'enseignement n'ont pas suivi cette évolution. Il est temps qu'un effort particulier soit fait dans ce sens.

Le titre de restaurateur dans la plupart des pays n'est pas protegé et qui veut, peut se nommer restaurateur. Ce n'est qu'en donnant une formation solide aux élèves dans les écoles de restauration que l'on pourra lentement éliminer de la profession les amateurs et élever la qualité moyenne des travaux de restauration.

78/22/8

TRAINING OF SPECIALISTS IN RESTORATION IN USSR

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Zagreb, 1978

TRAINING OF SPECIALISTS IN RESTORATION IN USSR

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Training of restorers in the Soviet Union is accomplished by the following institutions:

1) state higher and secondary educational institutions;

2) restoration organizations where students and graduates work on probation (it should be added that they are also sent abroad for this purpose);

3) qualification improvement institutes for creative workers of Ministry of Culture of the USSR where restorers may go through a course of training.

At present the following institutes and schools are engaged in training restorers: I.Repin Institute of Painting, Sculpture and Architecture in Leningrad, Kiev State Art Institute, Academy of Art of Georgian SSR, Moscow Art School In Memory of 1905 and Serov Art School in Leningrad.

Each of these institutions has a restoration department where students major in restoration of easel painting and monumental fresco and tempera. The complete course takes from four to six years and includes both theoretical studies and practical exercises.

At Moscow Higher Art and Industry School there is a department for training specialists in restoration of monumental and decorative painting, ceramics and furniture. Five or six month of the two-year course are given up to practical work.

At restoration departments of higher educational institutions the following subjects are studied: material technology and easel and monumental painting tech-

niques (244hr), special chemistry and biology course (154hr), applied physics and science of colour (62hr), plastic anatomy (124hr), descriptive geometry and perspective (124hr), special photography (94hr).

Much attention is given to art courses: painting and drawing (1700hr), graphic technique and copying (549, 6hr). Students are given lectures on history of Russian and world art, mythology and heraldry; in addition, there is a seminar where students study the Soviet law "Protection of historical and cultural monuments".

Studying of foreign languages occupies 248 hours.

600 hours are devoted to restoration proper; besides, annualy, beginning from their second year students are engaged in practical work at major restoration organizations. It is noteworthy that those organizations are not chosen on the location basis: thus students from Kiev and Leningrad often work in Moscow and vice versa. However, only fourth and fifth-year students may enjoy this form of work. In all, 50 weeks are devoted to practical work, that is about a working year's time.

It should be mentioned that students work not only in the offices of restoration centres, but also on a monument or in a museum as members of restoration teams where they are guided by highly skilled restorers not necessarily belonging to an institute staff.

In the course of practical work students gain experience in restoration, documentation and experimenting (chemical, etc.).

A diploma work usually includes restoration of two or three objects performed in different techniques and detailed restoration documentation. The task is determined by the student himself, but it needs an approval of the department scientific and methodological council

which also includes representatives of different restoration organizations. There are close links between restoration departments at institutes and restoration studios. The most qualified restorers give lectures to students, supervise them in their practical work and take part in the activity of scientific and methodological councils and examination boards. Central restoration organizations are supposed to issue restoration manuals, as well as methodological literature on training restorers and reviews of existing training methods.

Annually 35 to 40 students graduate from art institutes and schools. They are sent to work according to applications coming from different organizations.

At schools the program is structurally the same as at institutes, but since the whole course takes only some four years there, studying time is proportionally reduced and some subjects which are considered less important, such as heraldry, mythology, descriptive geometry, etc., are excluded. The program at Moscow Higher Art and Industry School leans to a purely technological side, but there, too, students study artistic techniques, copying and foundations of science of materials.

Perhaps, the most efficient method of restorers training is regular practical work at the central restoration studios. There restorers improve their skill by way of consultations and restoration work under a direct supervision of highly qualified proffessionals. All central restoration organizations, as well as restoration departments of major museums, take an active part in this form of training.

Work with probationers can be conducted in several ways, but the most effective method seems to be that using a single program of studies which purports to conduct training of restorers not only of different specialities, but also of different proffessional le-

vels. The All-Union Central Scientific and Research Laboratory for Conservation and Restoration of Works of Art (VCNILKR) recieves more than 60 probationers from different organizations annually. A program of studies is based on the applications that have arrived to the Laboratory during the previous year.

According to the present program probationers become attached to the Laboratory for the period of 5-6 years and work there one month a year. Groups are formed, subject to a proffessional level,each consisting of 6-8 persons. Each group has a highly qualified restorer as an instructor. When a study cycle is over a probationer is given a certificate where the operations that he has mastered are indicated and a recommendation is given for the next cycle. In a year he is summoned to the Laboratory again where he can, after presenting the documentation about the work he has done during that period, pass on to the following, more complex, cycle.

Probationers work both in VCNILKR and on a monument or in a museum. Such "outdoor" work may be done either on the initiative of the Laboratory or at the request of a museum. In the latter case an instructor should select, in advance, those exhibits that are relevant to the topic to be studied.

Probationers work not only in group, but also individually, by a special program. In most organization individual studies are conducted according to a previously developed plan. In the case of individual studies exhibits may be provided either by the organization involved or by a probationer himself.

Besides doing practical work in a narrow field probationers are engaged in the so-called "review" work, that is they work on a problem which is of inte-

rest to a number of restoration organizations. Every year Ministry of Culture of the USSR draws up a summary plan for probationers. Within that plan restorers from Algeria, Bulgaria, Romania, Mongolia and GDR worked on probation in Moscow and Leningrad.

Soviet restorers, too, improve their skill abroad.

Another form of training is seminars dedicated to most interesting achievements in restoration. Each seminar group consists of 25-30 restorers. The seminars last from one to two months.

The total number of probationers is 100-150 persons annually.

Nowadays, when restoration courses are read at educational institutions, the probation system has become a means of qualification raising rather than training beginners. In view of the fact that the problem of preserving cultural heritage is now becoming more and more important and of a rapid development of scientific methods in conservation and restoration the probation system seems to be growing in significance.

A great amount of work in raising restorers' qualification is done by qualification improvement institutes for creative workers of the All-Union and Republican Ministries of Culture.

Here a single program of studies has been worked out for all republican institutes. According to that plan, groups of 30 persons each are formed. First, lectures on foundations of conservation of object made of different materials are read to the whole of the group; then the group is divided into subgroups, each consisting of 6-8 persons. Within a subgroup practical studies in one single speciality are conducted. A one-month course has the purpose to acquaint museum restorers with basic preventive and conservation methods. This form of training is a great help to the museums

whose staff of restorers numbers only one or two men.

Qualification Improvement Institute of Ministry of Culture of Russian SFSR together with the I.E.Grabar All-Russian Art Scientific Restoration Centre has founded a qualification improvement school for inexperienced restorers from Russian SFSR. The two-year course consists of eighty days, forty days each year. Students become acquainted with methods used in the adjacent sections of restoration, general conservation, physical, chemical and biological methods of analysis. Practical studies are conducted in subgroups; other forms of work with the students include individual and group consultations, subject days, study of museum collections. Each restorer has its own plan of practical work, which is sanctioned by the the Restoration Centre restoration council.

Qualification improvement institutes also serve as a base for qualification improvement school for museum directors and curators; programs of those schools are also concerned with some problems of conservation and restoration. According to an order of Minister of Culture of the USSR, all restorers, regardless of their education, must recieve an approval of the State Restoration Qualification Committee of the Fine Arts and Monument Protection Board. The Committee, which was founded in 1954, estimates restorer's qualification in terms of four categories (3rd, 2nd, 1st and highest). For each category the character of work is defined. The final estimation is made on the basis of uniformal restoration documentation and the requirements for each category.

After being qualified restorers are given qualification certificates. These certificates remain valid only for a period fixed by the Committee, after which

restorers must be requalified.

The Committee consists of three sections, viz. painting section, drawing section and applied art and sculpture section. The documentation base is provided by VCNILKR.

Being a leading organization in conservation and restoration in the USSR, VCNILKR conducts the registration of restorers and reveals needs for restorers; it also plays an active part in restorer's training, distribution, qualification improvement and qualifying.

METALS

Coordinator : R.M. Organ (U.S.A.)
Assistant coordinator:
Members : E. Andersen (Denmark)
B.V. Arthur (Canada)
R.A. Bakhtadze (USSR)
C.W. Brewer (U.K.)
A. Escalera Urena (Spain)
M. Francaix (France)
A. France-Lanord (France)
M.K. Kalish (USSR)
C. Lahanier (France)
B. Leech (Canada)
J. Lehmann (Poland)
M. Marabelli (Italy)
E.M. Nosek (Poland)
C. Pearson (Australia)
C. Petersen (U.S.A.)
W.D. Richey (U.S.A.)
S. Saleh (Egypt)
F. Schweizer (Switzerland)
T. Stambolov (Netherlands)
R.E. Stone (U.S.A.)
B.N. Tandon (India)
V.P. Vinogradova (USSR)
L. Vlad Borrelli (Italy)

Programme 1975-1978

1. Procedures for electrochemical and electrolytic treatment (Organ).
2. Very simple methods of analysis (to be appointed).
3. Comparison of analytical methods and results (idem).
4. Corrosion-inhibitors: substances, advantages and disadvantages (Richey, Stambolov, Tandon, Pearson, Marabelli, Saleh, Vlad Borrelli).
5. The patination of bronze, natural, protection, synthetic (Kalish, Leech).
6. The corrosion and conservation of iron objects (Nosek, Pearson, Arthur).
7. Studies of the composition and fabrication of bronze objects (Escalera Urena, Brewer).
8. Use and mis-use of ultra-sonic treatment (to be appointed).
9. X-radiography and γ-radiography: methods and standardization (Stone, Lahanier).

10. Age-embrittlement and conservation treatment of silver objects, excavated or raised (Schweizer, Bakhtadze, Petersen, Andersen).
11. Identification of fakes and forgeries: methods and results (France-Lanord).
12. Conservation of modern materials, e.g. tinplate, magnesium (Pearson).
13. Conservation of modern materials, e.g. iron and copper in architecture (Lehmann).
14. Prevention of heat corrosion by inhibiting varnish (Vinogradova).

PLASMA REACTIONS IN THE CONSERVATION OF ANTIQUITIES

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PLASMA REACTIONS IN THE CONSERVATION OF ANTIQUITIES

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ABSTRACT

Low frequency (50Hz) alternating current has been used to produce a glow discharge in gas mixtures at low pressure. The chemical properties of the luminous portion of such discharges has been investigated. When the gases present are argon and oxygen, organic compounds may be removed from many substrates. Argon-hydrogen mixtures may be used in our apparatus to reduce several corrosion products back to their respective metals.

INTRODUCTION

Conservation techniques are frequently very laborious, and if chemical treatments are used to replace intricate manual work, it is difficult to ensure sufficent control and selectivity. In particular, liquids readily spread and penetrate into objects somewhat haphazardly and they will perhaps affect parts of the object in undesirable ways such as by causing swelling or by driving salts or other soluble components further into the object.

It seemed desirable to examine new methods of treatment which did not involve liquids. Exposure to gases and vapours seemed the only possibilites but generally their actions required heat to initiate chemical reactions, thereby altering or hazarding the objects. However, there is a means of enabling gases to become chemically reactive which does not involve heat. Electrical discharges produce ions and radicals which can be chemically very potent. Cleaning of surfaces and the reversal of corrosion seemed to be the prime requirement in conservation workshops, and our experiments have been directed to that end.

When a power supply is connected to two metal electrodes so that a potential difference is applied across a gas at low pressure, 10-100 Pa (1 torr= 133Pa) an electric current will begin to flow when the applied voltage reaches a critical value. As the current is raised its presence is made evident by light emission and the electrical phenomenon is called a glow discharge.

Glow discharges excited by d.c. (or alternating low frequency) power supplies have a region in which electrons are accelerated to energies sufficient to ionise gas molecules, and the positive ions so formed gain energy to eject electrons from the cathode electrode. Outside of this region is a luminous zone which is a gas plasma, in which the concentration of positive and negative charge carriers are

approximately equal [1]. Examples of plasmas in practical applications include the largest region of ionisation in neon and fluorescent lighting.

Gas molecules exposed to energetic particles can undergo dissociation or occupy metastable states.

Gases in which the plasmas are produced have enhanced and modified chemical properties compared with the same gases at room temperature and pressure. At low pressure the electrons, ions and neutral gas atoms (and molecules) can each attain different average energies arising from their mean free path and the discharge excitation. Thus, it is a system which can be characterised by several different internal temperatures and in which the prime gas remains relatively cool.

The novel chemical properties of plasmas were investigated as early as 1796 when it was found inter alia that ethylene could be polymerised [2]. Since then a large number of plasma reactions have been studied.

METHODS FOR PRODUCTING PLASMAS

As plasmas result from the passage of energetic electrons through a gas they can be excited using a heated cathode to release electrons into the gas as well as from a cold cathode exposed to positive ion bombardment. Another method of ionising a gas is to apply a radio frequency electric field to the gas so that electrons gain energy and oscillate in the gas under the effect of the field. As excitation is raised the electron energy reaches a level sufficient to ionise and dissociate gas molecules. Many studies of chemical reactions in plasmas have been made in r.f. exicted discharges and, plasma apparatus currently used for active gas reactions in the semiconductor industry commonly uses r.f. excitation. However, of all the available excitation techniques the most inexpensive is that using a cold cathode with a d.c (or low frequency a.c) supply. For the plasma region one would expect no basically different yield of chemically reactive components, but in the discharge sustained by formation of a space charge region of high electric field adjacent to the cathode, it is possible that highly energetic particles from that region may penetrate the plasma unless precautions are taken.

Apparatus. Glow discharges were produced inside a "Pyrex" 300mm diameter bell-jar sealed by a shaped rubber gasket to a steel base plate. This vessel was evacuated to less than 1.0Pa by a rotory pump plus liquid nitrogen trap. Gas mixtures were introduced from a tank through a needle valve until a pressure of 17-26Pa was produced whilst pumping. The discharge was excited by applying a voltage of 1.6kV across a pair of aluminium electrodes the leads of which were coaxially shielded by earthed aluminium tubes. The discharge was initiated at the U shaped section (fig. 1) where a glow was produced and directed mainly upwards. An aluminium mesh

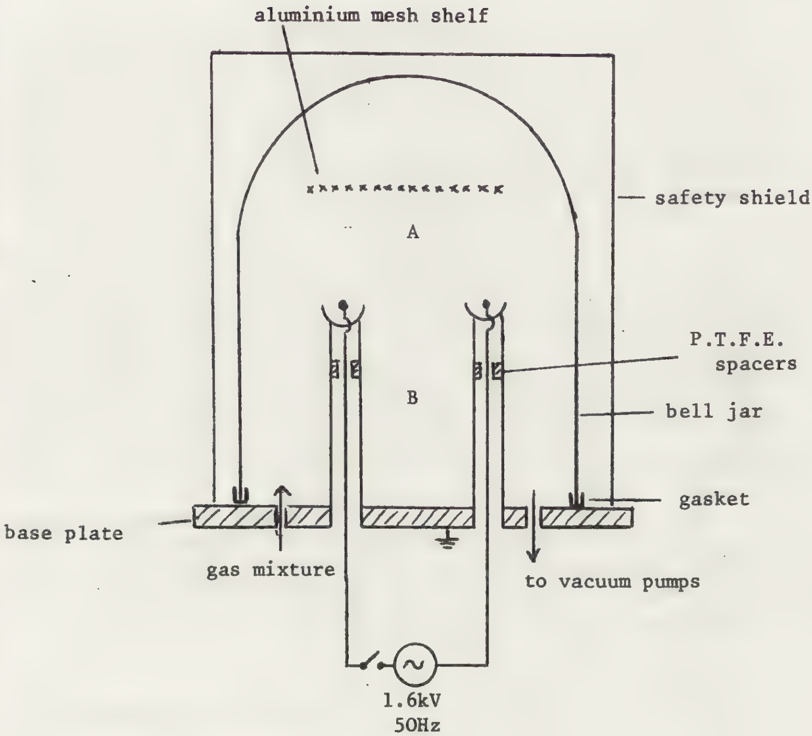

Fig. 1. The Plasma Reactor

shelf 100mm above the plane of the electrodes was set up for specimens (region A). The space below the plane of the electrodes will be referred to as region B. Power was produced from a supply fitted with a high reactance transformer. A vacuum safety switch was included so that the power would not operate without a vacuum in the belljar. Provision was made for the inclusion of a thermocouple, the resulting e.m.f. was led through the base plate using vacuum tight terminals.

Types of gases used. In principle any gas or vapour can be used to produce a plasma. Oxygen and hydrogen have been the first gases to be investigated because some of the properties of these plasmas were expected to be useful. These gases were diluted to 50%v/v by the addition of argon. Argon mixtures were chiefly used to minimise the explosion hazard, but the existence of metastable states in ionised argon can greatly contribute to the activation of the other gas. In the plasma energetic ions, atoms and molecules were present and in region A adjacent to the dark space zone some highly energetic electrons and scattered energetic neutrals may penetrate the plasma region, but they are not expected to pass 100mm to the specimens before losing their energy by collisions [3]. Most of the work was performed in region A because the reactions rates were faster than in region B. When operating, a mauve glow fills the belljar being more intense in region A. Around the electrodes, for about 30mm is the Aston dark space, the cathode layer and cathode dark space [4]. The rest of the glow is plasma in which no particles have high enough energy to sputter metals, but enough energy to be highly chemically reactive [5].

Plasma oxygen is capable of oxidising organic compounds at room temperature, to carbon monoxide and water. Plasma hydrogen is capable of reducing certain corrosion products to metal [6]. It was the aim of the experimental work to study these reactions with a view to using them for conservation.

1. Oxygen Plasma

A discharge was produced in 1:1 oxygen/argon plasma using 1.6kV 50H_z AC, a current of 23mA was produced at a pressure of 17 Pa as meaured on a Pirani gauge, In the plasma, near immersed objects, a thermocouple did not register a temperature of more than 50°C.

All organic materials immersed in plasma oxygen have been oxidised by this treatment. The only residue after oxidation is any inorganic material which may have been present in the organic material. This is easily brushed off a smooth surface. Results for the rate of removal of organic materials in region A are given in Table 1. The rate of removal of organic materials did not vary with time of treatment (zero order).

TABLE 1

Material	Density ($Mg m^{-3}$)	Rate of Removal $g h^{-1} m^{-2}$	Rate of Removal $\mu m h^{-1}$
Shellac (Heat cured varnish)	1.1	1.6	1.4
Araldite (AV/HV 100)) curedepoxy	1.14	3.3	2.8
Araldite (rapid) systems	1.14	3.7	3.2
Colloidal carbon (from aqueous dispersion)	-	2.0	-
Cellulose acetate	1.3	2.2	1.7
Nitrocellulose lacquer (Frigilene)	1.23	6.5	5.2
Poly(styrene)	1.05	2.7	2.6
Poly(ethylene terephthalate)	1.15	4.6	4.0
Poly(ethylene)	0.92	2.5	2.7
Poly(vinyl acetate)	1.2	3.4	2.8
Regenerated cellulose film	1.45	2.4	1.6
Poly(ethylene glycol) Carbowax 8000	1.1	2.5	2.3
Microcrystalline wax	0.9	1.4	1.6

Other materials examined are shown in Table 2. Optical microscopy was used in all cases to examine the materials exposed to plasma. Scanning electron microscopy was used to examine the metals exposed to plasma oxygen and the oxidation product of silver was identified by X-ray diffraction. The results show the effects of one hour in the plasma.

TABLE 2

Effects of O_2/Ar Plasma

Substance	Effect of O_2/Ar Plasma
Gold (24 ct)	No detectable change
Steel (Cu-steel)	No detectable change
Tin	No detectable change
Copper	Slight surface oxidation
Lead	Slight surface oxidation
Zinc	No detectable change
Silver	Extensive oxidation to Ag_2O(matt black)
Soda glass	No detectable change
Bottle glass - green	" " "
Bottle glass - brown	" " "
Pottery - Etruscan buchero	" " "
Pottery - Bronze age pot	" " "
Pottery - Greek black figure	" " "
Greek - white ground	" " "
Paper	Gradual erosion, no dis-colouration
Felt tip pen inks	Almost complete bleaching on all those tried

2. Hydrogen Plasma

A discharge was produced in 1:1 hydrogen/argon plasma using 1.6kV, 50HzAC. A current of 23 MA was produced at a pressure of 33Pa measured on a Pirani gauge. A thermocouple on the proximity of objects in the plasma did not register a temperature of more than 50°C. Surface of materials were examined before and after immersion in the plasma. Treatments lasting one hour in region A produced the effects listed in Table 3. The reduction product of haematite was indentified by X-ray diffraction.

TABLE 3

Effect of H_2/Ar plasma

Material	Effect of H_2/Ar plasma
Paper	Yellow/brown discolouration in region A but not in region B
Araldite (rapid and AY1000 system)	no detectable change
Shellac	"
Gold	"
Steel (Cu-steel)	"
Silver	"
Zinc	"
Lead	"
Copper	"
Tin	"
Soda glass	"
Bottle glass - green and brown	"
Pottery - Etruscan buchero	"
- Bronze age pot	"
- Greek black figure	"
- Greek white ground	"
Haematite	Reduced to black magnetite
Magnetite	no detectable change
Lead acetate)	
Basic lead carbonate)	grey coating on surface
Old corroded lead	blackening of surface which went brown overnight
Cuprous oxide)	
Cupric acetate)	
Malachite)	brown layer formed on surface
Paratacamite)	
Silver sulphide	reduced to silver
tarnished silver plate (silver flake in gum arabic Region B)	partially reduced to silver

Possible uses for plasmas in conservation

From the results it appears that hydrogen plasma has the ability to release lead copper and silver from some of their corrosion products, and to reduce haematite to magnetite. It would be naive to expect the corrosion product to yield metal with the same crystallographic and specular properties as the original metal. The corroded lead object gave what was probably a layer of lead metal with high surface area, but this was oxidised overnight to brown lead oxide.

The discolouration of organic compounds in region A of the plasma indicates that electron bombardment is responsible for this reaction, however, plasma treatment of silver, suspended in gum arabic, was partially successful in region B. Thin layers of silver sulphide can be successfully converted to silver, but thick layers although being completely reduced leave a slight opalescence on the surface of the metal.

Oxidising plasmas can be used to remove organic layers and stains which have hitherto been irremovable by conventional means. Clearly this treatment can only be applied when the substrate is resistant to the effects of the plasma.

Plasmas seem to react only with the surfaces of objects, and penetration into porous bodies is limited. However, sufficient plasma oxygen will penetrate 3mm into a 0.7mm gap and remove shellac completely from a glass slide. Although the penetrating power is far from being negligible it does mean that it is small enough for mechanical masking to be effective. If it is necessary for only part of an antiquity to be exposed to plasma, a mask can be cut out from another expendable or unreactive material, and provided a good fit is obtained at the edges of the mask ample protection is provided to the materials beneath. A particularly effective masking method is to paint on a lacquer such as nitrocellulose which is easily removable even after plasma treatment. By using this method extremely sharp boundaries can be obtained.

Future work

As yet only a few of the possible properties of plasmas have been investigated. The proportions of argon and reactive gas might be varied and different operating conditions such as pressure, potential difference and position in the plasma could be varied and other plasmas such as water vapour, carbon dioxide and carbon monoxide could be investigated. The cleaning of ceramic, glass and iron objects can now be attempted. The very high degree of cleaning possible should make significant improvements to the strength of adhesive joints in pottery and glass restoration. It is hoped that suitable operating conditions will be found so as to arrive at a useful restoration treatment for silver in illuminated manuscripts (leaf and paint) faded photographs and perhaps metal point drawings. The properties of alloys of various compositions in

plàsmas must be investigated so that the metal antiquities and coins can be treated. The size of articles that can be treated is limited only by the sàze of the containing vessel which can be provided, since the vessel itself can be easily fitted with plasma regardless of size. The outcome of these experiments gives good grounds for hope that plasma chemistry will reveal even more new treatments for antiquities in due course.

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SELECTING SAFE MATERIALS FOR USE IN THE DISPLAY AND STORAGE OF ANTIQUITIES

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SELECTING SAFE MATERIALS FOR USE IN THE DISPLAY AND STORAGE OF ANTIQUITIES

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ABSTRACT

The processes of corrosion of metal artifacts can be accelerated within the museum environment by the build up of corrosive vapours in the confines of showcases and storage areas. This problem can be alleviated by testing the materials used for their effect on metals.

We have examined the corrosive effects of several volatiles and considered a method for removing volatile organic materials from the atmosphere. An accelerated ageing test for materials has been reappraised and several modifications investigated. Many materials used in the construction of showcases and storage areas have been tested for their effect on lead and silver and the results of these tests are given.

The implications of this work on display and storage in museums is discussed.

INTRODUCTION

The corrosion and degradation of antiquities can be considerably accelerated by the presence of small amounts of harmful gases and vapours. Fresh air circulating around objects normally dilutes and removes vapours arising from materials, but to eliminate dust, maintain steady temperature and humidity and for security purposes it is often necessary to enclose objects as firmly as possible. Thus, there is a distinct possibility that harmful vapours arising from the materials of construction and display within a showcase can build up to levels which can cause corrosion and deterioration of the objects within the case. Recent work at the British Museum has been directed towards identifying and detecting such harmful vapours, understanding the processes involved and consequently screening materials to eliminate those which are undesirable.

The rate of deterioration of antiquities is dependent on many factors including temperature, humidity, mechanical damage, light and atmospheric pollutants. Thomson[1] has reviewed the effects of the major air pollutants on objects, and we recognise that further pollutants can be evolved into the storage environment from materials used in display, following Oddy's original publications[2,3] we have been screening various materials for use in storage and display, particularly with respect to metal objects where corroded surfaces can be particularly obvious and chemically active.

In considering the nature, origin and effect of some pollutant gases and vapours five particular and obviously separate species are reviewed and also miscellaneous organic compounds.

a. Hydrogen Sulphide (H_2S) Silver and polished copper are severely tarnished by hydrogen sulphide. There is a background concentration of $0.3\mu gm^{-3}$ naturally present in the air due mainly to rotting vegetation. Additional sources of H_2S are the protein materials such as wool, parchment and leather etc., because they contain sulphur in amino acids, cystaine, cystine or methionine. Silk however contains no sulphur in its protein material. Other possible sources of H_2S are sulphur dyes [4], polysulphide adhesives, improperly manufactured viscose rayon and vulcanized rubber, lead based pigments e.g. lead white and red lead are often blackened by H_2S. In normal laboratory air $0.3\mu gm^{-3}$ of hydrogen sulphide blackens silver at the rate of 6.0 nm per month. Watrous[6] has noticed in certain drawings that fresh silver point lines change from grey to brown corresponding to the change of silver to silver sulphide. Damage can also occur to silver photographic images. The black image turning light brown on exposure to hyrogen sulphide.

b. Sulphur Elemental sulphur vapour (vapour pressure at room temperature is 0.02 pa) damages antiquities producing the same effects as hydrogen sulphide. It is sometimes encountered as a gap filler or as sulphur objects (e.g. casts) or in vulcanised rubber.

c. Sulphur dioxide (SO_2) The major part of the sulphur dioxide in the air comes from the combustion of oil and coal. The effects of this gas are well known and as SO_2 is not liberated from the materials used in showcase construction it will not be considered further.

d. Nitrogen Oxides (NO, NO_2, N_2O) Small background concentrations of these oxides exist but there is no evidence to show that antiquities are attacked directly. Nitrocellulose in adhesives is a potential source of oxides of nitrogen if it were to breakdown. However there are no recorded cases of damage arising from this source, presumably because of the inclusion of stabilisers in the various nitrocellulose formulations. NO_2 is a catalyst for the conversion of sulphur dioxide to sulphuric acid which is so damaging to cellulose and protein materials.

e. Ozone (O_3) This highly reactive oxidising agent is formed in the upper atmosphere by ultra violet light, but can also be produced by improperly operating light fittings in showcases. Ozone will attack many organic compounds particularly those containing double bonds as in many conjugated natural colourings e.g. B carotene.

f. Organic compounds It has been known for many hundreds of years that oak can convert uncorroded lead metal into white lead which is basic lead carbonate, $2PbCO_3 . Pb(OH)_2$. The reaction which takes place is that of water and carbon dioxide with lead catalysed by acetic acid emitted by the oak. Corrosion will occur at concentrations of acetic acid as small as 1.3 mg m^{-3}. Other organic acids such as proprionic, n-butyric and iso butyric acids are similarly corrosive. Considerable work has been done on the attack of organic compounds on metals. Formic acid, also present in wood is not so corrosive as acetic acid. This effect is most marked with lead, cadmium, magnesium and manganese[8]. Other workers[9] have discovered that drying oils in air drying paints were responsible for the evolution of formic acid vapour and that hydrolysis of residual ester type solvents in paints and varnishes releases organic acids, mainly acetic. Chlorinated rubber paints are regarded with suspicion because of the possible evolution of hydrogen chloride. Some urea-formaldehyde and acid hardened phenol formaldehyde resins are corrosive to metals due to the suspected emission of fatty acids and formaldehyde. Poly vinyl acetate and cellulose acetate can release acetic acid by hydrolysis.

Several types of wood are highly corrosive to metals notably freshly cut oak and sweet chestnut. These woods are five times as corrosive as elm and ten times as corrosive as Norway Spruce.

Our own gas liquid chromatrography (GLC) studies of the air above wood samples show that acetic acid, methanol and methyl acetate were present in the woods examined.

In a detailed study of the composition of corrosive vapours emitted from wood Arni et al[13] have identified eight different compounds using G.L.C. in combination with other analytical methods. Their results confirm the fact that acetic acid is produced in greater quantity than other organic compounds, followed by formic acid at a factor of ten lower in concentration and then trace amounts of proprionic, isobutyric and butyric acids. Small quantities of ethanol, methanol and methyl acetate were also detected. Packman[14] has now detected formic acid in the volatile fatty acids, and has established that the acid contents of oak, Douglas Fir, Sitka Spruce, beech and birch increases in time due to the hydrolysis of acetyl groups in the hemicelluloses. Completely fresh, green oak wood did not contain measurable concentrations of acetic acid.

The general view of workers in this field is that all woods contain some free acetic acid, in addition more acetic acid may be liberated by hydrolysis of acetyl groups. Soft woods generally contain 1-3% acetyl groups while hard woods contain 3-6% acetyl groups.

Maximum evolution of organic acids occurs when wood is rendered down as sawdust. Wood in showcases and storage areas has a small surface area and the organic acids have to diffuse through to the surface of the wood before they can attack antiquities. Soft woods

are generally very permeable and unsuitable for storage of objects made of lead etc., but tropical hardwoods are relatively impermeable and do not evolve much acetic acid.

Many modern wood type materials are available and are composed of wood layers, blocks or chips held together by adhesives. In these cases the volatiles given off are probably a mixture of those given off by the woods and those given off by the adhesives (usually urea orphenol formaldehyde types).

ABSORPTION OF ACETIC ACID ONTO SURFACES

While developing techniques for sampling gas from storage areas it was found that acetic acid/air mixtures in the concentration range 260–2,600 mg m^{-3} change rapidly, the concentration of acetic acid dropping over 24 hours. Following the concentration of acetic acid vapour in sealed glass ampoules some of this was released again by introducing hydrogen chloride gas.

Using GLC it was shown that silica gel absorbs up to 4% $^{w}/_{w}$ of acetic acid before any residual acetic acid could be detected arising from the silica gel. When indicator was present in the silica gel the blue form i.e. dry silica gel was twice as efficient at absorption as the pink form. 10g of fresh blue silica gel was placed in contact with 100g of Oak Powder. After 24 hours the air above the wood was analysed by GLC, no organic compounds were detected by a flame ionisation detector i.e. less than 0.5 mg m^{-3} was present.

It would appear therefore that the acids released are also readily absorbed on alkaline surfaces such as glass. The absorbtion is strong but it is also expected to be limited. Emission over a long period of time might saturate the absorbtion capacity, consequently the use of high surface area materials with desirable absorbtion properties merits serious consideration. Recent work by Thomson[18] suggests that large quantities of silica gel are expected to stabilise the humidity within showcases but it seems that such a strategy may also result in the safe absorbtion of harmful vapours.

ACCELERATED AGEING TESTS

Accelerated ageing tests can always be criticized on the grounds that they do not accurately reproduce the reactions which occur during natural ageing. However an accelerated test is often a good guide to the corrosive effects of materials on metals.

For several years we have used the test described by Oddy [2,3] which can take four weeks to complete. In experiments to find a faster test several alternatives were tried.

A method is used in the textile industry to determine whether a material contains easily reducible sulphur. In this method a sample of the textile is boiled in a tube with a solution made by

mixing 10g of stannous chloride, 12ml concentrated hydrochloric acid and 8ml water. The evolved H_2S is trapped on a lead acetate impregnated paper covering the mouth of the test tube, a brown stain indicates the presence of easily reducible sulphur.[17] This test proved to be difficult to perform as the stain could be easily destroyed. The degree of staining being dependent on the way in which the solution was heated.

The preparation of silver pieces for use in the test described by Oddy was investigated. The tarnishing rate of silver prepared in the normal manner which was to degrease in cold acetone was compared with that of silver degreased with hot toluene in a soxhlet extractor and with fine silver as supplied. It was expected that the silver would be more effectively degreased with hot toluene in a soxhlet extractor and that the cleaner surface would tarnish more readily. In fact the tarnishing rate was the same for all three samples and preparation of pieces by degreasing in cold acetone was continued.

It was thought that the tarnishing might be accelerated by using very thin metal films. Lead and silver specimens were prepared by evaporating the metals in a vacuum onto glass microscope slides. This process produced bright lead and silver films but evaluation of the test was made impossible because even the small amount of corrosion produced in the control experiments, where no sulphur containing compounds or organic acids were present, was sufficient to cause a drastic change in the appearance of the test pieces.

Another approach to the problem was to use finely divided metal powders instead of metal foils. The results were assessed by microscopy. Changes on the metal appeared no earlier than on metal foil. It was therefore decided that there was no advantage to be gained by a change in the techniques of metal specimen preparation.

A variety of materials and their constituents have been tested over the years and some of the more interesting results are reproduced here. The method of testing is basically that described by Oddy. A sample (usually 0.5g) of the material was put into a 250ml quick-fit flask, 1ml of water was added to 1g cotton wool which was then placed in the flask and the flask stoppered. In the case of lead tests a 20mm x 20mm piece of Analar lead foil was inserted with 1g of solid carbon dioxide, and for silver test a piece of fine silver foil 10mm x 10mm was placed in the flask. The stoppered flasks were then put in an oven at 60°C for 4 weeks.

(i) Natural and Synthetic Polymers

Materials tested	Corrosion after four weeks	
	Silver	Lead
Radiation cross-linked polythylene	0	0
Viscose rayon	0	1
Terylene (poly(ethylene terephthalate))	0	0
Nylon 6	0	0
Nylon 66	0	0
Natural cotton fibre	2	1
Wool	2	0
Cellulose acetate	0	2
Poly (vinyl acetate) resin	0	2
Acrylic emulsion (Texicryl 13-002)	0	1
Poly (methyl methacrylate)	0	0
Nitrocellulose lacquer - Ercalene	0	0
Alkyd-nitrocellulose lacquer-Frigilene	0	0
Rubber (tubing)	2	-
Leather	2	-
Parchment	2	-

0 = no significant corrosion; 1 = some corrosion; 2 = serious corrosion

(ii) Woods

Several woods have been tested for their corrosion of lead. In these experiments a 5g sample of wood sawdust was used. The tests lasted for two weeks. Where the percentage of corrosion was measured, this was done by placing the initially weighted test piece in 25% cold acetic acid for five minutes to remove the basic carbonates. At the end of this time the lead was removed, washed in water and acetone, and reweighed. The extent of corrosion is the percentage of lead lost from the test piece.

Wood	Severity of Corrosion	Extent of Corrosion
Plywood (5ply; water soluble glue)	2	51%
Sundaela board	2	-
Beech	1	6%
Ash	1	8%
Oak (from timberyard)	2	19%
Oak (at least 10 years old)	1	7%
Elm	1	4%
Teak	2	17%
Larch	2	9%
Honduras mahogany	0	1%
Blank	0	1%

0 = no significant corrosion; 1 = some corrosion; 2 = serious corrosion

If Sundaela board (a type of chip board) is used in a real museum showcase it will tarnish silver within a few months.

DISCUSSION

Low levels of pollutants are always present in the atmosphere, but artificially high levels can be produced by the inclusion of certain materials in the proximity of some metal objects. The necessity to keep silver bright for display as demanded by many museums involves conservation staff in much work, and too frequent cleaning over a long period of time will inevitably lead to some loss of metal and rounding of surface detail. The alternative policy adopted by some museums of allowing silver to tarnish produces a different but not necessarily less aesthetically pleasing appearance and certainly involves less work on the part of conservation staff. However in the long term, the damage from sulphide attack may well be no less than from repeated decay and it would seem that in either case some means of delaying tarnishing must be found.

It is generally recognised that lacquering does not give adequate protection against organic acids or hydrogen sulphide.

Work on new protective coatings is in progress, but until a coating is produced care must be taken to choose showcase fabrics and other materials which do not liberate hydrogen sulphide or organic acids when susceptible metals are to be in the showcase. Much useful information could be gained by testing a wider range of materials such as the adhesives used to fix down the component parts of the showcases and mounts and the constructional material of the case itself, eg. wood, paints etc. It has been shown by our own experimental work and by previous reports that wood and paints can cause serious corrosion of metals.

In some cases by consideration of the chemical properties of a material it is possible to anticipate performance in an accelerated ageing test. It is not possible however to assume an industrially prepared material is safe using chemical knowledge because a manufacturer may introduce an unsafe ingredient. All materials should be tested before use.

Once pollutant vapours have been released their fate is a matter for speculation. Acetic acid is readily absorbed by glass surfaces due to reaction with the glass (chemisorption) and by physical absorption. Some of this acetic acid can be released by a substance with a stronger affinity for glass such as sulphur oxyacids. Cellulose and other organics have been shown to have a large capacity for absorbing sulphur dioxide and water, and it seems that this property is extended to organic acids. Hydrogen sulphide is susceptible to oxidation to sulphur, dilute solutions of hydrogen sulphide only last a few hours before the H_2S is oxidised to sulphur. Although large amounts of vapours are absorbed by surfaces there are still large amounts of pollutants which can be absorbed onto objects and react there.

The most dangerous situation for an antiquity is where it is completely surrounded by a material evolving harmful vapours, perhaps in a new wooded cupboard, in a plastic box or wrapped in plastic foam. Other hazardous situations are where objects trap air between metal areas and a damaging material, eg. a silver coin lying on felt. In these circumstances there is little chance for absorption of these vapours by any other materials. The answer is to either eliminate corrosive materials altogether or to isolate the object with an impermeable coating. Low humidity inhibits the corrosion of lead objects and good storage for lead could be obtained by using an inert container filled with dry silica gel which would not only absorb water but acetic acid as well.

Experimental work has shown that corrosion of lead can be caused by most woods, plywwod can be as harmful as oak to lead samples.

The Building Research Establishment have found the least corrosive wood to be mahogany. South American mahogany has been used with success in the coins and medals department of the British Museum, but it is gradually being replaced by safer materials. So far, no transparent finish for wood has been found that can usefully be used to cut down emission of volatile organic compounds. The search for easily worked, cheap and aesthetically suitable materials for showcase construction continues.

Metal foils are impermeable to the usual pollutants, and wooden boards can be coated with foil to eliminate emission of organic vapours into the air. However metal objects should not be in direct contact with foils so as to avoid the possibility of electro chemical contact.

Polyethylene foams have been shwon to be safe for storage and could gradually replace generally harmful polyurethane foams.

The complete elimination of harmful impurities in air is very difficult to achieve. Pollutants can enter an enclosure by diffusion and the expansion and contraction of air caused by temperature and pressure variations. Volatiles are liberated from some of the most frequently used building materials; wood, paints and adhesives. Careful selection coupled with testing of materials used should substantially reduce damage caused by pollutants, and absorbing materials could be used to trap harmful volatiles before they reach antiquities. An impermeable protective layer could be placed on antiquities to prevent access of harmful volatiles and there are signs that such a treatment may become available.

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METHODS FOR TREATING MARINE IRON

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METHODS FOR TREATING MARINE IRON

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ABSTRACT

In this paper a summary is presented of the marine iron treatment methods which have been studied and are currently being used at the Western Australian Museum. On-site conservation, transportation, stabilisation and display are discussed. The methods being used and the problems which may be encountered with them are briefly described.

INTRODUCTION

Over the past four years we have investigated many methods for the treatment of marine iron. These investigations have been concerned not only with the theory of iron conservation but also in the practical application of this to the conserving of marine iron artifacts.

In this paper we will briefly describe the marine iron treatment methods which we have studied and are currently using. Some of these are old methods which we have tested and found satisfactory, others have been modified to a greater or lesser extent or are entirely new. The full details of all these methods have either been previously published or are in the process of being published, and for specific technical details these works should be consulted. In this paper we will present a summary of the successful treatment methods and briefly indicate the problems which may be encountered with each.

The four stages of marine iron conservation can be considered as storage prior to conservation, stabilization through chloride removal, drying and finishing and finally storage or display of treated artifacts. Each of these stages naturally require different treatments and we will cover them separately in the above order.

A) STORAGE PRIOR TO CONSERVATION

This covers the period from the time when the surroundings of the iron artifacts are first disturbed up until the laboratory stabilization treatment commences. Maintaining the artifact during this period is generally the responsibility of the marine archaeologist or, if available, the on-site conservator. With all excavations it is essential to consider

storage and on-site conservation requirements during the planning of the expedition. (1)

Iron artifacts, when recovered from the sea, are nearly always covered with a layer of concretion. (2) This concretion, when intact, protects the underlying iron, to some extent, from chemical deterioration due to changing environments, and physical damage during handling. Consequently, concretion removal should not be automatically done on site but the alternative, of leaving the concretion intact until the artifact reaches the conservation laboratory, should be considered. In particular, cast iron cannon are much more safely stored on site and transported if the concretions are left intact.

There are two methods of iron storage which we have tried and found satisfactory. (3) These are:-

1. Wet Storage.

   Iron artifacts can be safely stored in a 2% solution of NaOH in water. It is preferable to use fresh water but if this is not available seawater can be used for periods of up to 6 months at least. If the concretion is completely intact the objects can be safely stored in fresh or seawater without NaOH for up to at least 6 months. For long term storage (greater than 6 months), 2% NaOH in fresh water should be used.

2. Dry Storage.

   For small artifacts only, storage by dehydration is possible. In this case the concretion must be removed and the object placed in a sealed glass container with indicating silica gel. A large quantity of silica gel must be used to achieve rapid initial drying otherwise damage will occur during the drying stage.

During the excavation, handling and storage of marine iron artifacts, particularly cast iron, it is crucial that the artifact is not allowed to dry out in the atmosphere. This relatively slow drying, even over a few hours, produces a concentrated salt solution in the pores of the graphitized zone. The resultant combination of plentiful atmospheric oxygen, finely divided graphite and metallic iron (cementite needles), and concentrated salt solution is ideal for extremely rapid corrosion. This can cause irreparable damage to the graphitized zone of the artifact very quickly. Consequently, when cleaning or examining iron artifacts in the field they must be kept wet.

The appropriate storage conditions must naturally be maintained during the transportation of the artifacts from

the excavation site to the conservation laboratory. This is particularly important for long transportation times. For obvious reasons it is difficult to transport large artifacts, such as cannon, in aqueous NaOH solutions. A satisfactory alternative is to pack the artifacts in wet sawdust, or cover with wet canvas, then wrap in plastic to maintain moisture and exclude oxygen.

B) STABILIZATION

The main aim of the stabilization process for marine iron is to remove the chlorides from the corrosion products. If these are not removed they catalyse the corrosion of the artifact, rapidly causing serious damage.

All of the treatment methods we are using involve, at some stage, the extraction of the chloride ions into a wash solution. In these cases it is essential to monitor the chloride ion concentration in the wash solution so that the progress of the extraction can be followed. From the chloride measurements, graphs of quantity of chloride released against $t^{\frac{1}{2}}$ are constructed which indicate both the progress of the extraction and, during the initial stages, when the wash solution needs changing. (4, 5) In all these processes the rate of chloride release from the artifact is controlled solely by the chloride diffusion rate in the corrosion product. Consequently any operation which increases the chloride diffusion rate will improve the treatment efficiency and reduce treatment time.

The following stabilization techniques have been used satisfactorily by us. However, when choosing a particular treatment method it is important to consider the limitations and difficulties of each method and the properties and condition of the artifacts being treated.

1. Simple Washing (4)

In this procedure the artifact is cleaned of concretion and immersed in a solution of 2% NaOH in water. The chloride content of the solution is monitored and the wash solution changed as necessary until the chloride extraction is finished. (4) As the chloride content of marine iron artifacts recovered from open sea sites is generally of the order of 10% b.w., ordinary tap water can be used satisfactorily for all except the last stages of washing when deionized or distilled water should be used. We have found no appreciable improvement in the chloride extraction rate when the solution was mechanically stirred or when it was maintained at low chloride concentrations throughout. Sodium carbonate and sodium sesquicarbonate have been used by some workers as an alternative to NaOH (14, 15). This is not recommended as both are significantly slower than NaOH in extracting chlorides from artifacts.

This is a very simple method which will, in theory, work for all marine iron artifacts. Unfortunately, except for lightly corroded objects, the treatment times are unrealistically long. Consequently this method should not be used where the graphitized zone of cast iron is greater than 0.3cm thick or the crevices in wrought iron are greater than 0.3 cm deep. The washing process can be accelerated to some extent by using a hot, not boiling, solution or by cycling the temperature between hot and cold several times.

2. Electrolysis (4,6,7)

The main effect of electrolysis is the reduction to magnetite of ferric compounds such as FeO(OH), Fe_2O_3 and FeOCl, which form the major component of the iron corrosion products. This reduction produces a decrease in the volume occupied by the iron compounds and a corresponding increase in the porosity of the corrosion products. As the porosity increases so does the rate of chloride diffusion through the corrosion product and into the wash solution. During electrolysis, no reduction of iron oxides to metallic iron occurs. In addition, the presence of an electric field has an insignificant effect on the rate of chloride ion extraction. In brief, electrolysis is a pretreatment of the artifact so that the simple washing, described above, can proceed more rapidly. In the case of wrought iron artifacts, a rapid evolution of hydrogen is deliberately produced during electrolysis as this removes residual concretions and loose corrosion products from the metal. Electrolysis works best for wrought iron artifacts which have a solid metal core but retention of the surface corrosion products is not possible. With care, electrolysis can also be used for cast iron artifacts provided a solid metal core remains. Electrolysis should not be used for completely corroded artifacts. A 2% NaOH in water solution is used as the electrolyte.

Due to difficulties in determining surface area and current densities through a corroded artifact it is better to use voltage rather than current control. A voltage of 4 volts, which causes vigorous hydrogen evolution, is used for wrought iron. With cast iron, 2 volts is applied for the initial 48 hours then the voltage is increased until H_2 evolution just commences (the current flow shows a rapid increase at this voltage which is generally between 2.3 and 2.5 volts). Rapid evolution of hydrogen from cast iron must be avoided as this will cause blistering of the graphitized zone.

Form fitting anodes are not essential but the anodes (mild steel is satisfactory) must have a large surface area and not be closer than 20 cm to the artifact. An exception to this rule is cannon barrels. In this case we use a mild steel anode rod inserted into the barrel, during the first 8 weeks of electrolysis only, to ensure reduction of the interior barrel surface. With cast iron artifacts, once the ferric compounds initially present are reduced to magnetite the continued passage of an electric current has very little effect on the rate of chloride release from the artifact. Consequently a repeated treatment cycle of 4 weeks on, 8 weeks off has proved just as effective, for cast iron, as continuous electrolysis.

The bulk of the concretion, including that in cannon barrels, must be removed before commencing electrolysis. Any small pieces of concretion which are difficult to remove without damaging the artifact may be left until electrolysis has been partially carried out. The electrolysis weakens the bond between the concretion and the artifact thus making removal of residual concretions easier.

It is essential to obtain good electrical contact to the metal of the artifact. With wrought iron this can be achieved by wire brushing clean an area to remove corrosion products then clamping the electrical leads onto this area. For cast iron artifacts it may be necessary to drill a small hole through the graphitized zone and into the metal core to obtain a good electrical contact.

Care must be taken to ensure that all surfaces of the artifacts are treated. Small objects should be suspended from wires and large objects, which need supporting stands, must be rotated. (8) The chloride concentrations in the electrolysis solution must be monitored as described above.

3. Alkaline Sulfite. (9)

This method is similar to electrolysis except that the ferric compound reduction is achieved by chemical instead of electrical means. This method is best suited for small, fragile or completely corroded objects when a H_2 reduction furnace is not available.

After treatment with the $NaOH/Na_2SO_3$ solution careful washing must be carried out to ensure that all the chloride and SO_3^{2-} are removed. As SO_3^{2-} ions interfere with the titrations for determining

chloride ion concentrations, the SO_3^{2-} must be removed or converted to SO_4^{2-} before analysing. This additional step makes the analysing slower and less accurate.

4. H_2 Reduction Furnace. (10,11,12,13)

In our procedure the artifact is heated in a stream of pure dry H_2 at 400°C for approximately 24 hours. For marine iron this lowers the chloride content to approximately 2% b.w. but more important, it reduces most of the ferric compounds to magnetite and metallic iron. This reduction produces a mechanically strong surface layer (particularly important for cast iron). The reduced corrosion products are very porous, being approximately 60% b.v. pore space. The residual chloride can thus be removed from them very rapidly by washing in a 2% NaOH solution; 4 weeks washing with weekly changes generally suffices.

This method has the additional advantages that any residual concretion which remains on the artifact after preliminary cleaning is degraded during the H_2 reduction. After reduction the concretion is soft and crumbly and can readily be removed. Provided the amount of concretion is not large it has no significant effect on the H_2 reduction of the artifact.

With this method, treatment temperatures greater than 400°C should be avoided as these can cause changes in the metallurgical structure of the artifact. (10) Pure H_2 should be used rather than N_2/H_2 mixtures as the latter are less efficient and require longer treatment times. It is essential that the H_2 entering the furnace is both dry and oxygen free.

After treatment the furnace must be allowed to cool to room temperature before artifacts are removed. Even when this precaution is observed we frequently find that the H_2 reduction produces pyrophoric iron on the surface of the artifact; that is, the artifact 'ignites' shortly after removal from the furnace. To avoid this problem we always have a container of 2% NaOH in water available and as each artifact is removed from the furnace it is immediately immersed completely in the NaOH solution.

The main limitation with H_2 reduction is one of size and cost. H_2 reduction furnaces are expensive although considerable savings can be made by converting an existing furnace using a stainless steel insert.

The operation of H_2 furnaces is safe when done carefully but if mishandled the results can be disastrous. For these reasons we treat large objects, such as cannon and anchors, by electrolysis rather than H_2 reduction.

In all treatment methods the most important feature to avoid is under treatment, that is, leaving residual chloride. It is a good practise, when possible, to analyse a sample of the corrosion product for residual chloride levels before proceeding to the final treatment stages. By trial and error we have found a residual chloride level of 200 p.p.m. or less to be safe whilst levels of 1000 p.p.m. or higher are definitely damaging. The levels used will depend on local storage conditions, in particular humidity levels.

Recently, the use of LiOH/alcohol wash solutions has been advocated for the removal of chloride from marine iron. (16) We have conducted comparative tests with this method and have found it to be of no practical value; at least for marine iron. The rate of chloride removal is significantly slower than in an identical washing using a NaOH/water solution. In addition the LiOH/alcohol treatment is more expensive, the health problem more acute and the fire danger higher.

C) WASHING, DRYING AND FINISHING

All the treatments described above result in an artifact which is practically free of chloride but which is saturated with a NaOH solution. To remove the NaOH and water the following four steps are carried out.

1. Immersion in deionized water for at least one week. No inhibitor is needed as sufficient NaOH is present in the artifact to inhibit corrosion.

2. Immersion in fresh deionized water for one week or more using chromate or nitrite inhibitors. These inhibitor concentrations (1000 ppm) are so low that negligible quantities are absorbed by the artifact.

3. For small artifacts, soak in acetone for 24 hours then remove and allow to dry. For large objects, paint on a copious excess of commercial dewatering fluid and allow to dry.

4. Immerse in, or paint on, a solution of 3% tannic acid in industrial methylated spirits as inhibiting agent against future corrosion.

At this point the objects are stable for indoor exposure for short periods. For long term stability, additional protection is required. The cast iron artifacts are consolidated and protected by immersion in molten

microcrystalline wax.(8) These remain totally immersed until all gas evolution from the metal ceases. The wax is then cooled until solidification just commences at which point the artifacts are removed. Excess wax can be removed from the surface using petroleum ether.

The wrought iron artifacts, after wire brushing, are painted with a primer (Kephos - Dulux Paints from I.C.I.) which consists of a phosphate corrosion inhibitor in a very low viscosity epoxy medium. Over this is applied successive, usually 3, coats of either a high durability clear acrylic (for indoor exposure) or a polyurethane paint (Imperite 390 - F & T industries) if the object may be outdoors for any appreciable time. In choosing a paint for outdoor exposure extreme care must be taken to ensure that the paint is not degraded by U.V. light.

D) STORAGE AND DISPLAY

For iron artifacts the ideal storage condition is zero humidity. This is not feasible as a museum environment, so the compromise value of 45 - 55% relative humidity is generally used. If the marine iron has been treated properly it will be stable indefinitely under these conditions. However, with all marine iron artifacts regular inspections must be carried out and if the indicating yellow droplets of $FeCl_3$ solution appear on the surface the artifact has to be retreated. If there are only a few small yellow drops, stability may sometimes be restored by simply washing the affected area with acetone. In more serious cases the paint or wax has to be removed and the artifacts completely retreated. Storage outdoors should always be avoided if possible.

CONCLUSION:

In this paper we have outlined the current marine iron treatment methods being used at the W.A. Museum. Full details of these treatments can be found in the papers referred to in the text. Provided the right treatment is chosen and the chloride analysis and monitoring is carried out, these methods should give consistently acceptable results.

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LA VERITABLE RESTAURATION D'UN BIJOU ACHEOLOGIQUE ET SA REPRODUCTION

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LA VERITABLE RESTAURATION D'UN BIJOU ARCHEOLOGIQUE EN EST SA REPRODUCTION

F. Marmolejo Camargo

Ce travail est le fruit de beaucoup d'anneés dans ma profession, plus de cinquante, et de mon attachement quand je faisais mes étúdes dans les écoles d'art sur des bijoux archéologiques. Lorsque ce trésor est apparu dans le "CORTIJO DE EBORA"(Sanlucar de Barrameda), j'ai en l'inquiétude de reconstituer ce dont seulement restait une dixième partie de la piéce laquelle, selon le professeur MATA CARRIAZO, avait fait partie des eléments apparus lesquels avaient une parfaite coordination de leurs articulations et seulement si on mettait de nouveau un fil d'or, la piéce restait echainée.

C'est d'ici que mon travail et c'est en reproduisant exactement l'original que j'ai complété la pièce comme la diadéme paseille à celle de "JAVEA" et de "LA ALISEDA".

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Grâce à la richesse en mines d'or et d'argent qui existaient dans la péninsule Ibérique et d'une manière plus concrète dans le Sud, l'Andalousie, aux moments de la colonisation par les peuples marins orientaux, d'une part, et immigrants de l'Europe Centrale, d'autre part, surgit au contact de ces deux courants et aux alentours des marécages du Guadalquivir la civilisation "Tartesia", créatrice des plus beaux bijoux archéologiques que l'on trouve aujourd'hui en Espagne, les trésors de Ebora et du Vstsmnolo, tous deux réalisés en or, et qui par leur perfection et leur beauté sont les témoins du haut niveau technique et artistique atteint par ce peuple, mais qui malheureusement et par suite de nombreuses vicissitudes nous sont parvenus, l'un incomplet et l'autre brisé et déformé.

Du point de vue de la conservation, étant donné la nature du métal noble, il n'y a pas de grands problèmes, mais si au moment de la restauration à cause des matières premières et de la technique de réalisation, (feuilles de métal très fines, soudures, etc.)

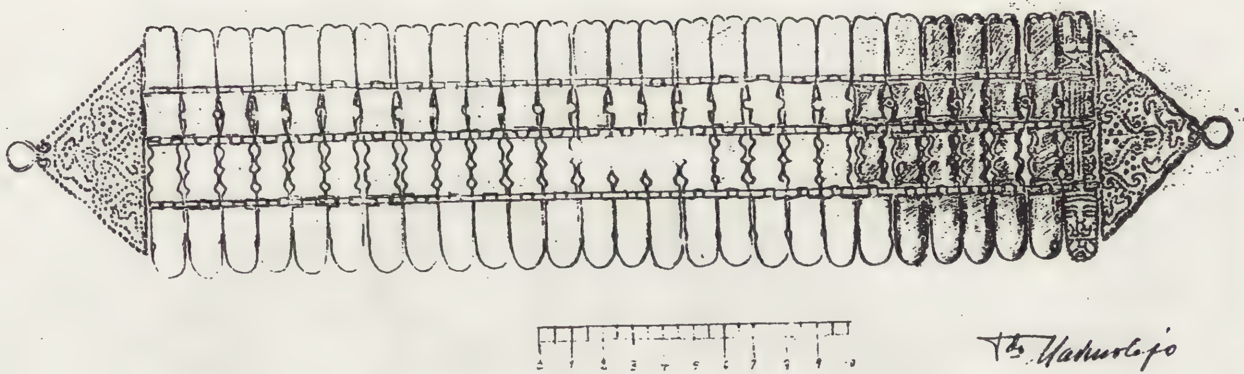
D'autre part, les bijoux archéologiques sont incomplets, même si ce sont des ensembles enfilés il manque fréquemment un grand nombre de pièces, et dans ce cas c'est le problème de la reconstitution qui se pose, comme pour tout autre type de restauration réalisée soit en prenant comme référence des pièces jumelles qui existent dans les musées, soit en ayant recours à l'imagination.

Il est évident que pour cette sorte de travail, en plus des études des historiens et des archéologues, il est nécessaire d'avoir une connaissance approfondie du travail de joaillerie d'un point de vue pratique et c'est la manière par laquelle le joaillier peut collaborer, et plus concrètement, c'est sa mission dans le monde de la restauration et de la conservation des bijoux archéologiques.

La téchnique de fabrication d'une pièce de joaillerie n'a pas varié depuis des milliers d'années; actuellement certaines opérations se font exactement comme aurait pu les faire un joaillier du VIème siècle avant Jésus Christ. D'autres techniques anciennes tombèrent en désuétude et disparurent totalement; il a donc fallu rechercher dans ces cas-là la forme dans laquelle elle furent réalisées.

En reproduisant une de ces pièces sur sa table de travail le joaillier dans la plupart des cas la solution à la question de savoir comment elle a été réalisée, car en posant le problème sur le terrain lui-même, les solutions sont, dans la plupart des cas, parallèles. C'est le cas de la reproduction du Trésor de Ebora, en arrivant à obtenir un granulé tel et comme il fut réalisé par les orfèvres "tartesos".

Si nous comparons, pour un moment, la restauration d'une toile avec celle d'une pièce d'orfèvrerie, nous pouvons voir que tandis que la première permet un travail limité à une zone, alors que le reste demeure pratiquement intact, cela n'est pas possible pour un travail fait sur du métal, car le simple contact d'un outil pour redresser une zone, éliminer une bosselure, etc. y produit un mal plus grand que le bénéfice que l'on peut en tirer. Evidemment, il n'est pas question de penser à appliquer le feu pour faire une soudure quelconque, ceci impliquerait l'utilisation d'acides et polissages par l'action desquels la physionomie de la pièce serait altérée, comme c'est arrivé malheureusement à beaucoup de bijoux appartenant à des collections très importantes.



DESSIN Nº 1: Dessin fait pour donner a la pièce les proportions de la diadéme de Jávea, avec les elements trouvés dans le "CORTIJO DE EBORA"(Sanlucar de Barrameda).

PHOTO nº 1 : Pièces d'or de la diadéme de Ebora, que grâce se trouver son assemblage et son fil parfaites conditions et être articuleé en forme de charniere, moyennant des petits tubes d'or sondés on a pu commencer sa reconstruction.

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PHOTO nº 2 : Fil des pièces trouvées, selon la disposition des petits tubes sondés sur les rhombes extrêmes de la diadéme. Ces rhombes avaient une parfaite coordination avec les forets qui traversaient les plaquettes et l'assemblage des mêmes.

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Les bijoux archéologiques sont restés dans beaucoup de cas enterrés pendant des siècles, soit dans des récipients de terre, soit directement au contact de la terre qui les couvrait, et qui sont précisément les mieux conservés parmi ceux qui sont arrivés jusqu'à nous, car ils n'ont pas été victimes de mauvaises restaurations ni de transformations de la part de joailliers inexperts. Puisque ces métaux étaient très convoités, les bijoux ont été enterrés et ont subi une action chimique superficielle appelée patine, qui les a embellis encore plus en les recouvrant de ce mystère caractéristique de toute pièce archéologique,mais elle a également subi d'autres actions mécaniques qui ont altéré sa physionomie, coups, bosselures, cassure. Sans doute, n'importe quel agent physique ou mécanique altère profondément son aspect, c'est pourquoi on ne peut penser en la restauration de ces sortes d'oeuvre d'art, critère qui heureusement coïncide chez les archéologues et les restaurateurs.

Que peut-on faire alors pour pouvoir voir l'oeuvre complète, dans son intégrité? Car le manque d'éléments réduit sensiblement la valeur de la vision intégrale du bijou et en conséquence de sa beauté; pour cela la reproduction exacte, basée sur les pièces en notre possession a donné un résultat très satisfaisant. Un simple fragment peut être suffisant pour voir comment il a été réalisé, voir tout l'aspect technique de sa réalisation et en collaboration avec l'historien spécialisé on peut obtenir la reproduction complète de l'oeuvre.

C'est le cas des trésors "tartesios" de Ebora et du Carambolo, du trésor Wisigoth de Guarrazar, les épées de Saint Ferdinand et de Boabdil, et d'autres encore.

Grâce à ces reproductions, pour lesquelles il a suffit de photographies, d'esquisses des originaux et de quelques mesures, on a même pu indiquer leur utilisation primitive, en arrivant à les substituer aux originaux dans des expositions où les bijoux authentiques auraient pu se trouver en danger. Les reproductions ne sont jamais réalisées en métaux nobles (or et argent) mais en d'autres métaux de ductilité semblable, comme par exemple le cuivre, étant ensuite recouvert d'un bain d'or, et en obtenant au moyen de patines et d'oxydations une ressemblance maximun avec les pièces originales, et on arrive ainsi avec un total succès, à atteindre les buts pour lesquels ils on été réalisés.

PHOTO nº 3 : Reproduction en cuivre doré de la diadéme faite avec la même façon que l'originale et en pouvant observer une grande flexibilité dans ses pieces.

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STRUCTURAL CHANGES IN ANCIENT SILVER ALLOYS: THE DISCONTINUOUS PRECIPITATION OF COPPER

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STRUCTURAL CHANGES IN ANCIENT SILVER ALLOYS: THE DISCONTINUOUS PRECIPITATION OF COPPER

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ABSTRACT

The age embrittlement of ancient silver could be due to discontinuous precipitation of copper from the supersaturated silver-rich silver-copper solid solution during the long sojourn at ambient temperatures. Microstructures of a number of ancient silver samples (500 BC to 600 AD) have been examined with the optical microscope and by microhardness measurements. The microstructures are compared with the precipitation behaviour of modern, artificially aged silver-copper alloys. Based on kinetic data the growth-rate of the precipitating cell at 25 C is estimated to approximate 10 μm/year. The temperature-dependence of the interlamellar distance of the segregated copper in the precipitated cell could be used to distinguish between ancient objects (aged at ambient temperatures) and artificially aged modern objects (aged at elevated temperatures).

1. INTRODUCTION

It is well known that certain ancient silver objects are found to be in an extremely brittle state after they have been excavated and brought into museum collections. The brittleness can be observed on objects which are corroded but also on those which show little or no signs of external corrosion. Knowledge of the causes of embrittlement is of great value for the conservation and restoration of deformed objects as they have to be made ductile before any reshaping can be attempted. Several methods to consolidate brittle silver have been proposed[1-4]. From the metallographical point of view the brittleness of ancient silver represents an interesting problem, as the change from a ductile to a glass-like brittle alloy implicates changes of the microstructure of the silver artifacts. Thompson and Chatterjee[18] examined the brittleness of ancient silver coins and came by practical experience to the conclusion that the precipitation of lead in the alloy was mainly responsible for the brittleness. C. S. Smith,[5] however, based on work by Norbury[6] and others attributed the embrittlement to the presence of copper which introduces an instability. The constitution diagram of the binary

silver-copper system shows that silver will hold a fair amount of copper in solution at the eutectic temperature (8.8% by weight) but only about 0.1% at room temperature (fig. 1). By quenching, the precipitation of copper is suppressed. The decomposition of the unstable super-saturated solid solution can be initiated in a few days or even hours by subsequent tempering at elevated temperatures. It is accompanied by an increase in hardness. Based on hardness measurements by Cohen[7] at various temperatures Smith suggested that the precipitation of copper from the supersaturated solid solution could occur even at roomtemperatures in periods of a few centuries[5]. A general review of age embrittlement of ancient silver has been published by Werner.[3] He distinguishes three main causes: intercrystalline corrosion, age- or precipitation-hardening and large grain size.
To investigate further microstructural changes in ancient silver-copper alloys, the research laboratories of the Musee d'art et d'histoire in Geneva and the Metropolitan Museum of Art in New York have set up a joint research project. One of the aims of our project is to study if there are any significant differences between "naturally" age-hardened and "artificially" age-hardened alloys. Although in both cases the decomposition of the supersaturated solid solution may have started, it can be expected that the morphology of short or long term precipitated phases may differ. We hope that this study will lead to a new approach to distinguishing between ancient and recently made silver objects. The detection of faces should then be possible even if ancient silver had been remelted, artificially corroded or age-hardened.
After initial work by scanning electron microscopy of the surface morphology of an ancient broken silver sample the microstructures of a number of silver samples dating from 500 BC to 600 AD have been examined and their microhardnesses determined. The literature on the precipitation of copper in silver-copper alloys has been reviewed.

2. THE DISCONTINUOUS PRECIPITATION OF COPPER FROM A SILVER-COPPER SOLID SOLUTION

2.1 General

Precipitation phenomena and hardening of silver-copper alloys were discovered more than 50 years ago. Early work by Norbury[6], Agew et al[8], Barrett et al[9], Jones and Sikes[10], and Gayler and Carrington[11] treated the metallography of aged silver-rich copper silver-alloys and their physical properties (hardness, electrical conductivity) and X-ray diffraction studies. It could be shown that supersaturated silver-copper crystals decompose by two different types of copper precipitation. At high temperatures and low supersaturation the copper precipitates in general within the grains along crystallographic planes and the X-ray lines gradually move from their original position corresponding with the supersaturated solid solution to new positions corresponding

with the equilibrium composition at the ageing temperature. This type of precipitation is called "continuous". At low ageing temperatures and high supersaturation the precipitation starts normally on the grain boundary and the precipitated cell grows with a sharp reaction boundary into the grain. The original lines in the X-ray spectra decrease in intensity and at the same time new lines appear, corresponding with the stable solid solution, which increase in intensity until the lines or the original solid solution disappear. This type of precipitation is termed: discontinuous. The decomposition of the supersaturated crystal occurs at the reaction boundary and as it migrates an aggregate of precipitated phase and depleted solid solution is formed behind the advancing interface. This aggregate is characterized by a regular (cellular) arrangement of the precipitate and depleted matrix phase. The depleted matrix phase has the same crystallographic orientation as the grain from which it grew[12] (fig. 2).

2.2 Morphology

The morphology of discontinuous precipitation of silver-copper alloys has been studied by transmission electron microscopy by Leo[13]. He showed in 1957 that in its early stages discontinuous precipitation is preceded by "zone formation". Copper atoms are concentrated in the form of very thin plates on the (100) plane of the silver matrix. The formation of "zones" was first postulated by Cohen based on hardness measurements. Discontinuous segregation of the supersaturated solution takes place only as a second step. A number of interesting theoretical papers on cellular precipitation have been published in the proceedings of the Detroit meeting on "Cellular and Pearlite Reactions."[14]

2.3 Micro-and Macro-hardness

Since 1925 the influence of quenching-rates, deforming grade and heat-treatments on the hardness curve have been intensively investigated[6-12]. The most interesting work has been published by Scharfenberger et al.[12] The authors compare the microhardness with transmission electronmicrographs during the formation of precipitated cells (fig. 3).

The first increase of the microhardness in the unprecipitated areas is due to the formation of (continuous) zones (see 2.2). Shortly before visible discontinuous precipitation sets in the microhardness decreases slightly to rise to its maximum value. The microhardness of the precipitated cell changes very little as precipitation proceeds. The macrohardness is consistently higher than the microhardness of the different phases even when the whole microstructure has recrystallised.

2.4 Kinetics

Isothermal transformation curves for a silver-5.5 wt% copper alloy aged at 200 C have been determined first by Rose[15] in 1957. Pregel and Rude[16] examined the accelerating or retarding effects of a number of elements alloyed to a silver-copper matrix. The discontinuous precipitation of copper is accelerated by the addition of 0.5 at% Ga and retarded by additions of equal amounts of In, Tl and Pb. No discontinuous precipation could be induced in a binary silver-lead alloy. Scharfenberger et al[12] investigated the discontinuous precipitation of cold worked sterling silver at temperatures between 200 and 500 C. Three successive migration rate stages could be distinguished. Small migration rate changes at the beginning of the discontinuous precipitation, fast decrease and subsequent decrease during completion of discontinuous precipitation. The most recent publication is by Diekstall[17] on discontinuous precipitation in tri-crystalline specimens of silver- 6.2 at % copper.

3. MATERIALS AND METHODS

3.1 Ancient silver samples

Table 1 shows that about 14 samples have so far been selected. They represent a wide variation of silver-rich silver-copper alloys. As not all samples had been taken with this study in mind, the pre-treatment (e.g. annealing for restoration) of some of them is not known .

3.2 Preparation and ageing of modern silver-copper alloys

Modern silver alloys have been prepared artificially by melting the appropriate amounts of silver, copper, gold and lead in a graphite crucible under reducing conditions. Their composition has been adjusted to match the average composition of Byzantine silver. The samples have been chemically analysed (table 2). Prior to ageing, the samples were solution treated for 2 h at 720 C in a graphite crucible under a layer of charcoal in a electric furnace and quenched in ice-water. They were aged in the same way at the appropriate temperature.

3.3 Preparation for metallographic examination

The fragments were mounted separately in a cold setting epoxy resin, rubbed down on different grades of emerypaper to grade 600 and polished on a slowly rotating wheel with fine suspensions of alumina on a cloth lap. We found it difficult to bring out the microstructure by etching. We obtained the best results by swabbing the etching solution with cotton wool rapidly over the

polished samples (5-10 times). We could reveal some structures only after repeated etching and polishing cycles. The etching solution consists of a stock solution containing 100 ml saturated $K_2Cr_2O_7$+ 2 ml sat. NaCl + 10 ml H_2SO_4 conc. This is diluted 1:9 with water. We found it best to prepare the diluted solution twice a day. The stock solution lasts 2-3 weeks.[3]

3.4 Microhardness

All measurements were carried out with a Reichert microindentation tester.[19,20] The load was kept as small as possible (3.3 gram) to minimize the diagonal of the test-point (8-9 microns). The reproducibility is approx ±6%.

4. RESULTS

4.1 Microstructures of ancient silver samples

The microstructures of all samples have been recorded by a number of microstructures of all samples have been recorded by a number of micrographs. These were taken in areas which showed little or no corrosion. The results shall be presented here only in terms of the shape of the grains and the boundaries and the presence or absence of any visible precipitation of copper. Almost all microstructures showed evidence of cold working and annealing. Based on these criteria we separated them into four broad groups.

4.1.1 Microstructures with apparent grain boundary displacements ("jig saw puzzle type")

A number of samples (MAH 75-263-7, 8, 1, 30c, 31a MMA-SS26) showed a very characteristic appearance (fig. 4). At low magnification the boundaries have a wiggly, jagged appearance. At higher magnifications some of the grain boundaries appear double. Others have very strange curved outlines (fig. 5). This is the type of microstucture which has been observed and described by Smith on a Sasanian head[21] and a Romanesque reliquary[22] and by Werner on a Persian anklet.[23] We looked particularly at the distorted grain boundaries for any evidence of precipitated copper. If the grain boundary displacement is due to the discontinuous precipitation of copper during the long sojourn at room temperatures, we would expect the cellular structure to be within the indentation. With the optical microscope at magnifications up to 1200X we were not able to see cellular structures. Characteristic for this group is the small grain size of 0.01 to 0.04 mm.

4.1.2 Microstuctures with large grain size

Two samples (MMA-116 and -SS24) have particularly large grains (up to 0.2 mm). SS 24 is of some interest as neutron

activation analysis gave a copper content of 0.15% only. The grain boundaries of these two samples are in general straight. These large grains must have been formed after the last high temperature anneal by secondary recrystallisation. They compare well with Werner's cross-section of a Persian anklet.[24] SS 24 shows some dark patches along the grain boundaries which have not yet been identified.

4.1.3 Microstuctures with visible precipitation of copper

Two samples show some evidence of copper precipitation. The type of lamelar structure of the center of sample MAH 75-263-1 and MMA 187 is, however, typical for discontinuous precipitation which has taken place at elevated temperatures (see discussion).

4.1.4 Annealed samples

Silver samples which have been annealed during restoration are, as expected, not suited for metallographic studies of this kind. Whereas some microstructures revealed the presence of high-temperature precipitation (continuous), others are fully recrystallized (MAH 75-263-3r, -7r, -9r and probably MMA-LE).

4.2 Microhardness

Of particular interest are microhardness measurements on silver samples of microstructure-group 4.1.1. It can be argued that the microhardness in the middle of the grain and within the indentation created by the displaced boundary should be different if the displacement is accompanied by discontinuous precipitation of copper. The results of the microhardness measurements in table 3 are not conclusive. Sample MAH 75-233-31a does in fact show slight but consistent higher values for "indentation areas". This difference is, however, not noticeable in samples MAH 75-263-7 and -8 and "indentation areas" even have a lower microhardness. This is interesting as both samples show very pronounced features of grain boundary displacement. In general the microhardness is higher than that of solution-treated and quenched samples but lower than that of artificially aged specimens.

5. DISCUSSION

Almost half of the ancient silver samples examined have microstructures with very pronounced grain boundary displacements. They are of the same type as those described by Smith[5,20,21] and Werner[3]. This "jig-saw puzzle" microstructure is apparently unique to ancient silver alloys. Similar microstructures have,

as far as we know, not been observed on artificially age-hardened silver copper alloys. The absence of this type of microstructure is, however, not an indication that the sample is not ancient.

The presence of discontinuous precipitated cells along the grain boundaries could not be ascertained by observation with the light microscope. Some grain boundaries do etch in a double line and show small dark patches. At magnifications up to 1200x we could not reveal cellular structures. Examinations with the scanning electron microscope are now in progress. Some grain boundaries have a very curved outline and etch as fine dark lines. We have considered the possibility that the "noses" in the grain boundaries are areas of invisible discontinuous precipitation. The precipitated cell would correspond to the area enclosed by the curved grain boundary (reaction front) and its original position. Microhardness measureents within these areas gave readings similar to those in the middle of the grains. We were interested to estimate the rate at which discontinuous precipitation of copper occurs at room temperatures. In fig. 6 we have extrapolated the results of Scharfenberger et al[12], Rude and Pregel[16] and Diekstall[17] for various silver-copper alloys. Linear extrapolation gives a maximum growth rate of 10 μm/year. This means that in a Byzantine silver alloy from the 6th century (equal to 1400 years BP) the reaction front could have migrated approximately 1.4 μm. The discontinuous precipitation of copper does, as has been shown by Diekstall[17], not set in immediately but only after an incubation time. The incubation time depends on the ageing temperature. Extrapolating Diekstall results on tri-crystalline silver-copper alloys to room temperature we can expect an incubation time between several centuries up to 2000 years. No work has so far been reported on incubation times of polycrystalline material.
We have compared the observed grain boundary displacements with the size of the expected precipitated cells at room-temperature. The size of the dark patches along the grain boundaries is about the right order of magnitude (if we ignore the incubation time). The "noses" discussed above are, however, too big for precipitated cells. In addition they don't etch as areas with discontinuous precipitation normally do. At present we are not in a position to explain their formation. It could be that they are areas where recrystallisation was retarded by inclusions on the grain boundary. Scanning electron micrographs (taken by the Department of Inorganic Chemistry, University of Zurich) on a sectioned ancient silver sample have in fact shown the presence of refractory inclusions.
It is quite clear that any large patches of discontinuous precipition (10 μm) which are present in microstructures of silver-rich silver-copper alloys must be due to precipitation which has occured at elevated temperatures. Fig. 6 shows that between 300 and 500 C the growth rate of the cells is considerable.

The investigation of the lamellar structure of discontinuously precipitated cells offers a very interesting possibility for the authentication of ancient silver objects. As the distance between the precipitated copper lamellae is temperature dependent[17,25] it should be possible to distinguish between precipitation which occured at ambient temperatures and beginning precipitation at elevated temperatures. The latter may have been induced artificially to "age" the objects. It could also be the result of annealing operations.

Finally, discontinuous precipitation of copper has some implications for the restoration of ancient silver. It would be very dangerous to anneal brittle silver in the temperature range between 250 and 600 C as the alloy would be hardened by precipitation of copper. Annealing has to be done well above 600 C and the silver has to be quenched to avoid any precipitation.

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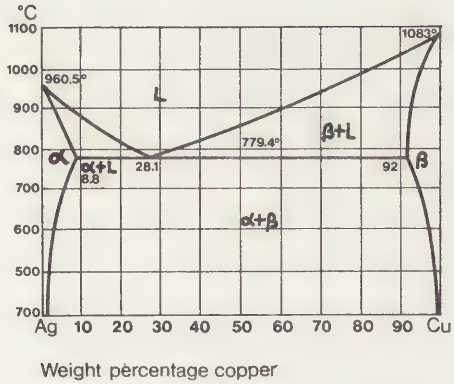

Fig. 1 Constitution diagram of silver-copper alloys

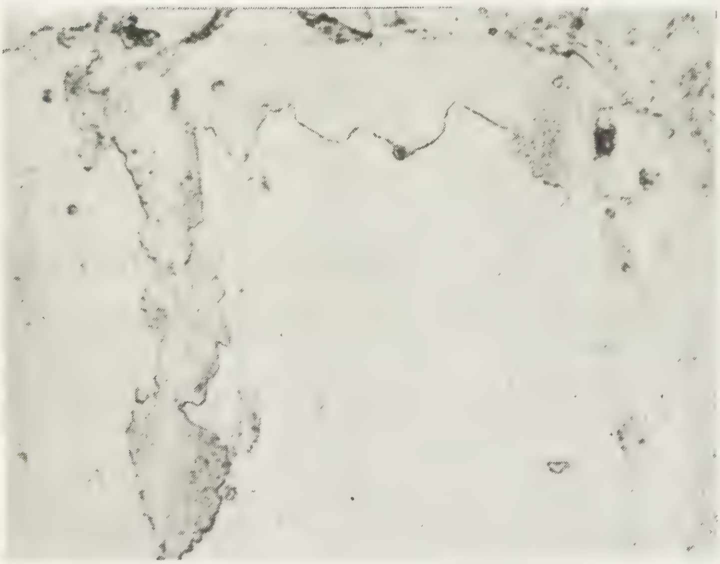

Fig. 2 Discontinuous precipitation of copper in a silver-5.0 wt % copper alloy. Aged 210 min. at 280 C. 700x

Table 1 List of ancient silver samples

Code	Period	Copper and lead contents Cu %	Pb %
MMA-SS24	Hellenistic	0.15	n.a.
MMA-SS25	"	3.04	n.a.
MMA-SS26	"	6.46	n.a.
MMA-LE	Sasanian	7.5	0.39
MAH-75-263-1	Byzantin 6th C. AD	4.6	0.6
MAH-75-263-7	"	3.5	1.1
MAH-75-263-8	"	1.9	1.0
MAH-75-263-30c	"	4.5	0.7
MAH-75-263-31a	"	n.a	n.a.
MMA -116	Byzantin	3.0	n.a
MMA -187	modern ?	4.2	n.a
MAH 75-263-3r	Byzantin	2.1	0.8
MAH 75-263-7r	"	3.6	1.0
MAH 75-263-9r	"	1.8	0.4

MMA = Metropolitan Museum of Art
MAH = Musée d'Art etd'Histoire
n.a = not analysed

MMA : Analysis by Neütron Activation
MAH : Analysis by X-ray fluorescence

Table 2 Modern silver alloys

Code	Composition in wt%				Ageing temp. °C	Ageing time hours
	Ag	Cu	Au	Pb		
MAH St.						
3-1	94.95	5.05	-	-	280	3.5
3.2	94.95	5.05	-	-	280	84
MAH St.						
6.1	93.5	4.55	0.95	1.0	280	3.5
6.2	93.5	4.55	0.95	1.0	280	86

Table 3 Microhardness (Hm) of ancient silver samples

Code	area	Hm near displaced grain boundaries kg/mm^2	Hm in grain middle kg/ mm^2
MAH 75-263-31a	d	90 ± 5	80 ± 5
	e	77 ± 5	72 ± 4
	f	83 ± 4	61 ± 5
75-263-8		84 ± 5	85 ± 5
75-263-7		74 ± 4	80 ± 5
MMA - 116		80 ± 5	75 ± 4

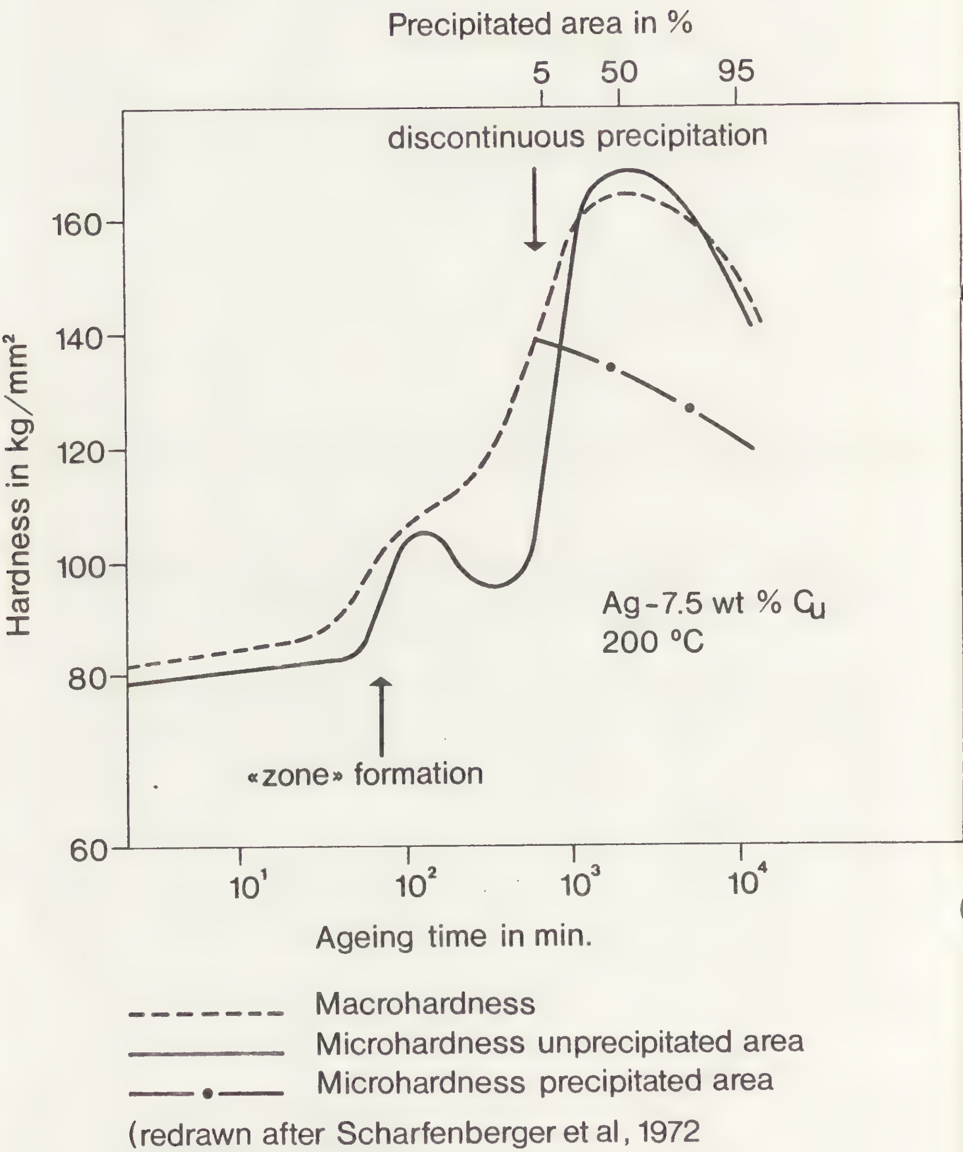

Fig. 3 Time-hardness curve for a silver -7.5 wt% copper alloy aged at 200 C.

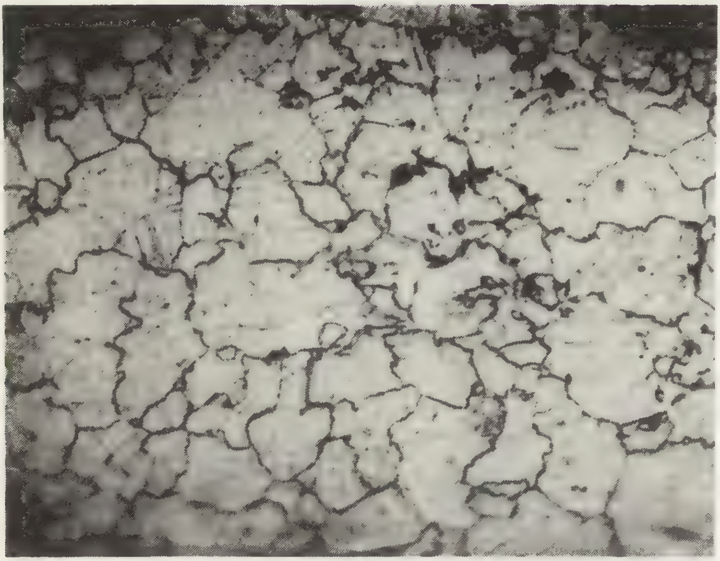

Fig. 4 Microstructure of a Hellenistic silver dish (MMA - SS26). 600x

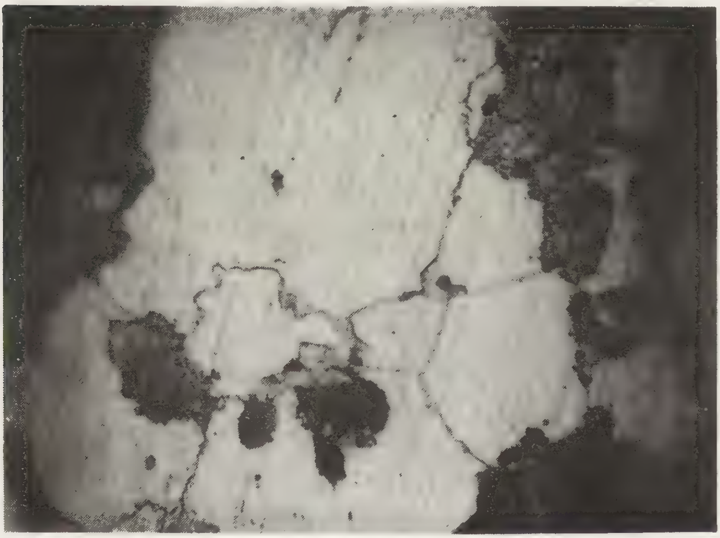

Fig. 5 Microstructure of a Byzantine silver spoon of the 6th Cent. AD. (MAH 75-263-8)
Note the grain boundary of the center grain. 1200x

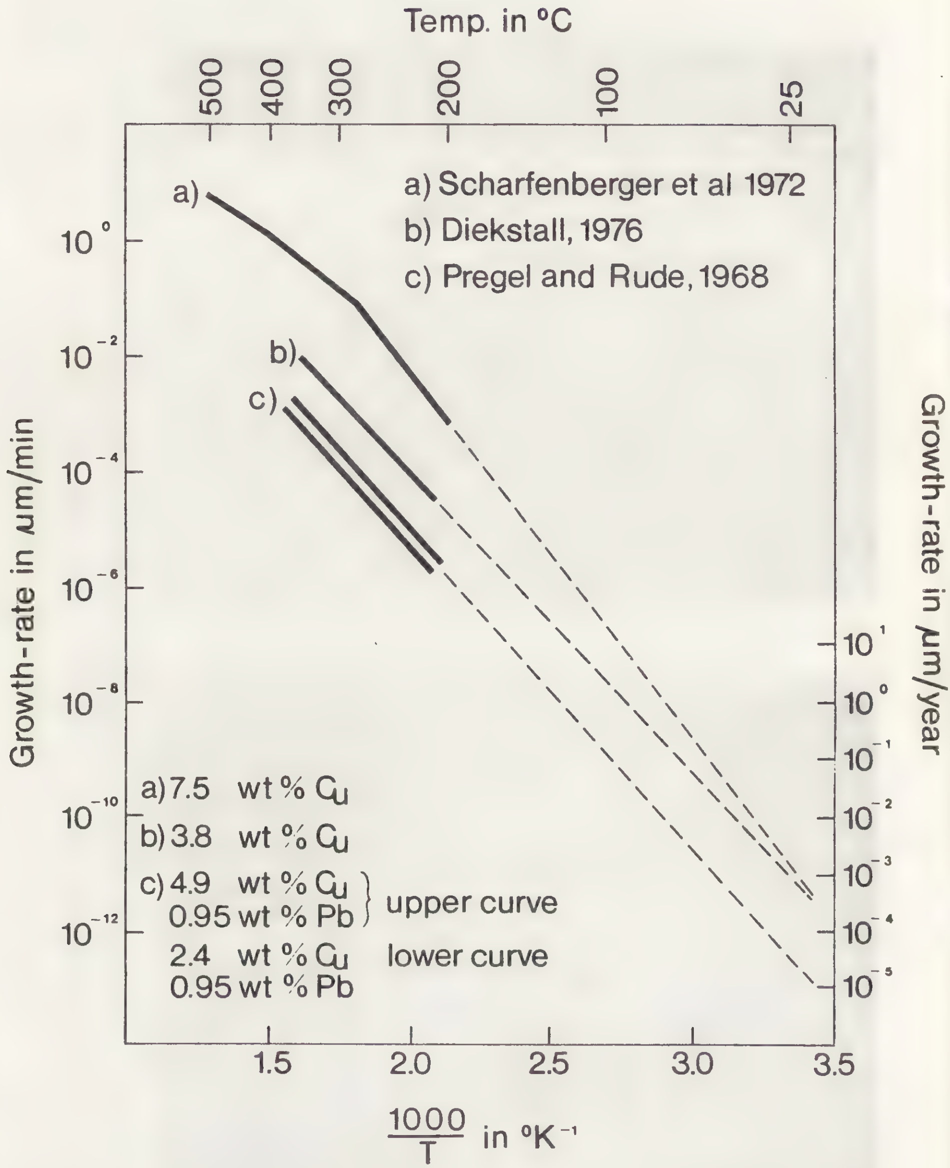

Fig. 6 Curves showing the expected growth-rate of the discontinuous precipitation at ambient temperatures

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A NEW COMPOSITION OF PATINA FROM THE ROOF OF THE WAWEL CATHEDRAL

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A NEW COMPOSITION OF PATINA FROM THE ROOF OF THE WAWEL CATHEDRAL

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ABSTRACT - Results are presented of chemical and x-ray diffraction analyses of samples of corrosion products taken from the gilded objects on the surface of the Sigismund chapel cupola and the roof of the Wawel Cathedral in Cracow. This research has allowed us to establish the origin of this corrosion of bronze objects and to identify the composition of the corrosion products, as well as to determine the influence of the atmospheric pollution on the patina.

1. INTRODUCTION

The renaissance Sigismund chapel of the Wawel Cathedral in Cracow was erected in the sixteenth century by order of king Sigismund the First and executed by the Italian architect Bartholomeo Berreci.

The chapel was built on the basis of the square and topped with a cupola covered by tiles hammered in the form of carp scales and gilded by the mercury amalgam method. The cupola has a round lantern at its top. Above the top of the lantern the crown with arches can be seen and on the pedestal is placed a kneeling putto holding a small crown above its head topped with an orb and cross. Both putto as well as the small crown and cross are cast in bronze while other elements are made of sheet copper and are also gilded.

2. THE STATE OF PRESERVATION OF THE OBJECTS

The surmounting elements of the lantern were found to be in a very bad state of preservation. The surface of the metal, especially the bonzes, revealed numerous corrosive pittings, cracks and gaps. It was discovered that the objects made of sheet copper suffered damage to the gilding. The gilding of the cupola was destroyed in 60 percent out of the total of 2500. Only 52 tiles were completely preserved. Many of these defects were present as deep, narrow gaps filled with the products of corrosion. The more seriously damaged tiles were covered with a green - greyish layer of corrosion products about 0.5 cm thick in places.

3. INVESTIGATION

In order to determine the causes of the corrosion as well as to establish some methods of conservation it was necessary to perform several preliminary examinations. Samples of corrosion products were taken from the objects surmounting the lantern as well as 10 samples of the patina from the gilded tiles. For the metallographic and chemical examinations, samples of metal were taken.
Additionally, samples of patina were taken from the nearby roof of the cathedral.
To compare chemical compositions of the old and new patina an experiment was made. Test samples with similar compositions to those of the original sheet metal were placed on the roof. All these examinations have not been completed yet and will require microanalysis tests but preliminary results have been obtained so far.

3.1. CHEMICAL ANALYSIS

Chemical analysis was conducted by a spectrographic method and in the case of the bronze objects several microanalyses were carried out to determine the lead content using the Kevex-Ray microanalyser. Table 1 shows the results. It is evident that the bronze objects are characterized by a large non-homogenous chemical composition and are high in copper. The sum of the alloying elements does not exceed a few per cent. The non-homogeneous content of the metal is presumably the result of the dendritic segregation which occurred during casting. Copper sheet which constitutes the basis of the crown, as well as the sphere and cupola, contains up to 2 per cent of lead.

3.2. EXAMINATION OF CORROSION PRODUCTS

X-ray diffraction analysis was carried out in order to determine phasal composition of corrosion products.
Chemical analyses to assess the quantity of soluble and insoluble chlorides and sulphates were also made.
The X-ray diffraction analyses were performed using Tür 62 diffractometer /CuK radiation/. A phase was considered only if at least three characteristic peaks had been observed. Table 2 shows the results of these investigations.

3.3 METALLOGRAPHIC EXAMINATIONS

Three samples were examined-taken from the sphere, tiles of the roof and a fragment of the small crown. Observations revealed a layer of corrosion products forming a characteristic adhesive between gilding and the copper base. In the damaged places corrosion products were identical on both sides. Metal structure was homogeneous. It resulted from reheating the alloy up to 500°C for gilding.

4. RESULTS AND DISCUSSION

a - Among the grey and green corrosion products in the bronze objects, brochantite $Cu_4/OH/_6SO_4$, anglesite $PbSO_4$ and a slight amount of malachite $Cu_2/OH/_2CO_3$ were dominant.

b - In the material from the copper sheet of the Cathedral roof, brochantite, atacamite and cupric fluorides were detected.

c - In samples nos. 1, 3, 4, 8, 10, 14 cupric fluoride was also found.

d - The green patina found in the narrow gaps of the tiles on the cupola consisted for the most part of malachite and a small amount of brochantite.

e - The brown and black patina under the gilding contained cuprous oxide (cuprite).

f - In the light - greyish samples taken from the bronze objects, lead sulphate was identified, resulting from lead corrosion (electrochemical attack of lead in the alloy). Microanalysis for the lead alloy content, as well as differences in the lead appearance on the surface, bottom and side walls, seem to confirm this conclusion.

g - The black patina on the crown arches and the small sphere contained magnetite Fe_3O_4. It resulted from the corrosion of the iron metal parts supporting the cap construction.

h - Basic copper chlorides - atacamite - were discovered in the samples nos. 3, 10.

i - Tested samples of sheet metal were covered during one year by a layer of patina consisting of copper sulphates, sulphides, a small amount of chlorides and cupric fluorides. The amount of the soluble salts was significantly larger than in the material taken from the cupola.

j - In the dark - blue patina on the small crown at the bottom of the cupola, $CuSO_4 . 5H_2O$ was detected. The patina on the crown resulted from crystalisation of soluble salts and not from sheet corrosion. Corrosion appeared only in some convex places on the small crown.

k - Gypsum was found in samples nos. 3, 8, 9.

From the results obtained so far it may be concluded that the patina on the roof the Cathedral consists mainly of basic copper sulphates. Its origin is largely sulphur dioxide present in the polluted atmosphere. The amount of SO_2 in the atmosphere surrounding Cracow is very high. During the autumn-winter period it reaches 130 $^{mg}/m^3$.

In November 1977, pH measurements of condensed water on the cupola were made. The water pH ranged from 4.5 to 5.5. Rainwater partly washed out the patina from the surrounding roofs.
Fluorine responsible for the formation of cupric fluorides was also detected in the polluted atmosphere. The appearance in the patina of cupric fluorides is the result of fluorine emission into the atmosphere by an aluminium plant located in the vicinity of Cracow. From recent data it appears that the amount of fluorine in the air is approximately 30-70 $\mu g/m^3$, 40 per cent as gas.
The research on the fluoride patterns in the patina is in progress.

TABLE I

The results of chemical analyses of some objects from the cupola:

Area of Sampling	Elements wt %					
	Pb	As	Fe	Mg	Au	Cu
Putto/body on the surface with damaged gilding	0.5	0.20	0.20	-	0.3	98.8
Putto/body near the crack	0.4	0.25	0.15	-	0.02	99.3
Putto/body, bottom of the crack	2.70	0.15	0.15	-	-	97.0
Putto/left leg surface near crack	0.6	0.15	0.10	-	0.05	99.1
Putto/left leg, bottom of the crack	1.21	0.20	0.10	-	-	98.49
Crown with arches	1.15	0.15	0.25	0.8	-	97.65
Small Crown a/surface	0.4	0.20	0.20	1.15	-	97.85
b/wall of the crack	0.6	0.25	0.15	-	-	99.0
c/bottom of the crack	4.8	0.20	0.20	-	-	94.80
Tile from the Cupola a/base	1.10	0.10	0.11	0.8	-	97.89
b/gilded surface	0.12	0.50	0.01	1.21	95.66	2.5
c/damaged surface	0.98	0.10	0.10	0.75	0.20	97.90

TABLE II

The results of X-ray diffraction analysis

Sample	Type of patina/place of setting	Cuprite Cu_2O	Malachite $Cu_2/OH/_2CO_3$	Brochantite $Cu_4/OH/_6SO_4$	Antlerite $Cu_4/OH/_4SO_4$	Atacamite $Cu_2/OH/_2Cl$
1.	Light green/putto arm	++		++		
2.	Light grey/body of putto					
3.	Greyish green sphere	++		++		+
4.	Green/cross	++		++		
5.	Black brown/cross under gilding					
6.	Black/big crown					
7.	Black/big sphere					
8.	Light green/copper roof of the Wawel	++			++	
9.	Light green/tile bottom of the narrow crack		++	+		
10.	Green/tile with the defective gilding	++		++		+
11.	Green/tile	++	++			
12.	Black brown/under gold leaf	++				
13.	Green/tile	++		++		
14.	Green blue/crown at the bottom of the cupola	++		++		
15.	Dark green/on the convex place, crown at bottom of the cupola	++		++		

TABLE II cont.

Sample	Type of patina/place of sampling	$CuSO_4.5H_2O$	Anglesite $PbSO_4$	CuF_2	Magnetite Fe_3O_4	Gyps um
1.	Light green/putto arm		+	+		
2.	Light grey/putto body		++			
3.	Greyish green/sphere		++	+		++
4.	Green/cross			+		
5.	Black brown/cross under the gilding					
6.	Black/big crown				++	
7.	Black/big sphere				++	
8.	Light green/copper roof of the Cathedral			+		++
9.	Light green/tile bottom of the narrow crack					
10.	Green/tile with the defective gilding			+		++
11.	Green/tile					
12.	Black brown tile under gold leaf					
13.	Green/tile			+		
14.	Green blue/crown at the bottom of the cupola	+				
15.	Dark green/crown at the bottom of the cupola on the convex place					

78/23/6/6

78/23/7

REDUCTION THERMIQUE DES OBJETS CONFECTIONNES EN FER ENTIEREMENT CORRODES OU PRESQUE

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Zagreb, 1978

REDUCTION THERMIQUE DES OBJETS CONFECTIONNES EN FER ENTIEREMENT CORRODES OU PRESQUE

Božidar Vilhar

Je voudrais exposer ici une méthode de conservation pratiquée dans notre institution, dictée tout d'abord par la proximité des eaux salines et puis à cause du manque des installationes apropriées.

Presque tous les objets en fer de l'époque préhistorique, et du haut moyen âge où trouvés au cours des missions sous-marines, présentent ce même aspect de l'oxidation totale, souvent même avec une cavité à la place de l'objet disparu. L'exception en sont dans le plupart des cas les objets de l'époque romaine, probablement à cause de la meilleur qualité de fer ou de l'acier employé, ainsi que tous les matérieaux en fer à partir du XIV ème ou XVème siècle. Dans ce cas une réduction électrolytique suffit. Ces objets sont transformés, en leur totalité ou presque, en mineral de fer: FeO, Fe(OH)2, combiné avec $Fe\ Cl_2$. A leur surface se sont aglomerés en masse compacte et sourvent très dure, sable et terre environnants donnant à l'objet une forme souvent méconnaissable. Trouvés en mer, à la surface du fond ce sont en général des incrustations calcaires. Une identification aux rayons X n'est pas difficile, mais reste incomplète en tenant compte du fait que nous cherchons à rendre à l'objet sa forme originale reconnaisable et à empêcher sa destruction à cause du brusque changement du milieu.

En 1968 j'avais l'occasion, au cours de mon séjour en Suède et en Danemarque faire connaissence au département de conservation du Musée maritime, avec des resultats obtenus par Lars Barkman sur la réduction de fer par hydrogene et à Kopenhagen de la méthode Rosenberg, pratiquée par Boërge Brorson Christensen.

Faute des appareils à l'hydrogène nous avons adopté la méthode Rosenberg modifiée en tant que nous lui ajoutons au cours du procès de chauffement la réduction à l'oxide de carbon au moyen du charbon de bois pour éliminer ainsi l'oxigène et tous les autres élements néfastes pour l'éxistence durable de l'objet en question.

La méthode à l'hydrogène a cette avantage qu'elle est plus rapide: le long lavage après la réduction n'est pas Nécessaire du tout. Notre méthode n'exclut une réduction à l'hydrogène postérieure.

Description de la methode

L'objet en fer est débarassé au moyen d'une brosse douce, des particules non adhérantes. Selon le cas, une radiographie aux rayons X est effectuée. Si la surface montre des traces de bois, de cuire ou de textile, elle est entièrement enlevée au moyen de laque à base de celulose soluble, en deux ou trois pièces. Ces pellicules sont ensuite rassemblées avec de l'Aradite et nous recuperons de cette façon une copie exacte de l'objet comme il se trouvait en moment de sa découverte, avec sa surface originale conservée. Débarassé de tout ce qui aurait pu être intéressant pour sa documentation il est enveloppé entièrement par une cordelette d'amiante, qui épouse bien sa surface. Par dessus vient encore une protection en fin fillet de fer le tout renforcé par un mince fil de fer. Si l'objet, à cause de sa longeur, comme un couteau par exemple, tend à se casser pendant l'opération de réduction, on le renforce le longue de ses contoures au moyen d'un fil de fer plus epais. Tout ce travail protège l'objet contre une désintégration possible au cours des brusques changements de température. La réduc tion s'effectue dans un four électrique en présence d'un excès de charbon de bois. La température s'elève progressivement à 800^{o}C pour y resté stationnée pendant une heure. Ensuite encore incandescents (750^{o}C), les objets traités sont plongés dans une solution saturée de soude caustique, portée à l'ébulition durant 2 à 6 heures, suivant le volume de l'objet. Par la suite on le fait bouillir dans de l'eau distillée pendant 12 heures. Suit un nouveau bain porté à l'ébulition d'une solution de 50 cm^3 de soude caustique dans 150 l d'eau distillé pendant 24 heures. Ce lavage intense enlève de ce fer reduit a l'état spongieux et enrichi de carbon, toutes les sels et elements devenus solubles. Après encore un bain d'une heure dans de l'eau distillée pure et bouillante on place les objets encore humides dans un bain de parafine, porté a 125^{o}C, où ils restent jusqu'à la disparition de l'efferevesence produite par l'évaporation de l'eau. On les enlève de ces bains à une température inférieur à 80^{o}C pour retenir dans leurs pores le plus de paraffine possible. Apres le refroidissement toutes les protections métaliques sont enlevées. L'amiante rest intimement lié à la surface du métal réduit et remplit les creut de sa surface. La recherche et la libération de la forme primitive s'effectue a l'aide de la radiographie préalablement faite. La surface originale n'est pas difficile à suivre, toutes les incrustations et dépôts s'étant ramolis. L'apparition des grains de sable blancs sur le fond noir de la masse superficielle aide à guider la main du conservateur. La où nous avons seulement une cavité à la place du noyau de fer disparu elle est déjà remplie de paraffine avec par dessus une mince couche de la surface originale.

Résultats:

Depuis 10 ans nous pratiquons cette méthode, avec des résultats assez satisfaisants, surtout quand nous sommes en présence d'un autre métal enrobé dans la masse oxidée de fer. Ces restes fins d'ornement, de bronce pour la plupart, sont aussi reduits a l'etat metallique. Détecté par la radiographie ils sont aisément rendus visibles à la surface libérée. La couleur rouge des objets traités par la méthode

Rosenberg est remplacée par le noir métallique pas trop désagréable à l'oeil, et qui donne sensation qu'on est en présence d'un fer récemment forgé. Coté negatif de la méthode: avec le temps ça et là apparaît une tache blanchâtre, vraisemblablement de la soude caustique qui était laissé en minime quantité avec le but de protéger le fer.

L'extrême fragilité des objets réduits n'est pas trop consolidée par l'impregnation dans la paraffine.

Notre but à atteindre serait de remplacer la paraffine, après le nettoyage et la libération de la surface de l'objet, par une matière platique qui lui donnerait une plus grande solidité. Les recherches dans cette direction sont seulement à leurs debuts mais nous avons déjà eu de très bons résultats en remplissant avec de l'Araldit les creux des pièces, non réduites thermiquements, découvertes au cour des missions archéologiques sousmarines. Il a suffit de casser les incrustations pour que la forme primitive aparaisse.

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SPOT TESTS IN CONSERVATION:
METALS AND ALLOYS

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SPOT TESTS IN CONSERVATION: METALS AND ALLOYS

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Abstract

A short project initiated in the Analytical Research Services laboratory of the Canadian Conservation Institute had as its objective, development of quick and reliable spot tests which can easily be used by conservators on metal objects. A set of tests for the qualitative determination of Au, Cu, Fe, Sn, Zn, Pb, Ni and Sb have been distilled from the literature and from those tests presently used by conservators. Minimal damage to the object being tested can be achieved through a combination of electrolytic sample collection, spot test papers available commercially, and the standard microchemical tests; the procedures found to be optimum are described.

Introduction: Sampling

The sampling restrictions particular to museum objects complicate spot test procedures. Whether the test is performed directly on the artifact or a small sample is removed, one must minimize damage to the object and recognize that the results are not necessarily indicative of the composition of the whole object. For example, plating and surface enrichment effects must be considered.

The majority of commonly used spot tests involve one of the following sampling methods:

1. application of a drop of solution which will dissolve a small amount of the surface metal, and reaction of subsequent test reagents in situ[1]
2. removal of this dissolution drop by capillary tube, pipet or glass rod to a filter paper, glass slide, or other place for further testing[1-6]
3. taking a streak of metal on unglazed porcelain and doing further reactions on the porcelain surface[1]
4. other methods of physically removing a piece of the metal, such as filing or drilling.[1,6,7]

Less common variations of these methods were not studied.[8-11] Two additional techniques have been developed more recently, and in fact are commercially available in limited forms.[12,13] These methods can significantly enhance the effectiveness of the spot test, while at the same time doing minimal damage to the object. They are:

5. application to the metal surface of a filter paper previously impregnated with reagent, and moistening of the paper with water, an acid, or a base (this may or may not make a slight mark on the surface)

6. electrolytic removal of a sample onto moistened filter paper, where test reagents can then be applied.

Initial Experiments

Methods 1-4 were investigated first. The disadvantages of some of the processes involved (such as drilling) are obvious, due to their effect on the object. Taking a metal streak as a sample was not found to be very successful in these experiments. The best overall results were obtained by the application to the object of a small drop of acid or base. A review of the literature and consultation with conservators produced an extensive list of candidate spot tests for various metals. Numerous experiments were performed under varied conditions in order to derive the set of tests which provided the most consistent results (see Table 1). In the case of Ag and Pb, a complete test could be performed on the object, since the very vividly coloured precipitates obtained stood out well enough on the metal surface to be easily distinguished. For the other metals, removal of the drop to filter paper was the best method.

The application of a drop of acid or base to any important object must be closely controlled. Unless the surface is carefully degreased (this can be done with acetone) or if the surface is rough and corroded, the drop may spread out and become a menace to the object's appearance. Further, it is generally a good idea to observe the dissolution process carefully. The reactions involved may be very slow, and visible perhaps as a darkening of the metal under the drop, or an etching effect. A feeling for when the reaction has proceeded far enough that an appreciable quantity of metal has gone into solution, is eventually acquired. For example, if one were analyzing predominantly Sn with traces of Cu and Pb, in order to detect the Cu, the reaction must proceed much longer than needed to detect the Sn.

Throughout these first experiments, disposable pipets were used for the application and removal of drops. With these pipets (equipped with a rubber bulb for better control of the liquid) a drop of 1-2 mm in diameter can be placed on a surface. This can be done consistently with practice. Smaller drops can be

obtained by drawing out the tips of these pipets over a flame, and breaking off the narrowed tip at a smaller diameter. In general, a drop size of 1 mm is optimum, since a microscope should not be required equipment for this type of test. A 1 mm drop can be observed for reaction with the unaided eye. A small hand-held magnifier would, however, be a definite aid in reducing the scale of the test while preserving its practicality.

In cases where there is doubt about what the coloured reaction should look like, a common sample containing that particular metal can usually be located close at hand for a comparison test. In this work, each test was done on pure metal foils of all the other metals being investigated, to check for possible reactions giving the same result. Objects containing a mixture of elements were also used for this purpose.

The principal disadvantages of these techniques are apparent in two areas. First, the tests can significantly mark the object because of the difficulty in localizing the spot and because of the prolonged contact required to collect sufficient sample for reliable results especially for minor constituents. Secondly, the tests are sometimes slow and inconclusive because of decomposition of organic reagents and somewhat inconvenient due to the large number of liquid reagents necessary to test for different metals.

Improvements to Test Methods

During the course of the experiments, two modifications were investigated which proved to be extremely useful. The first is listed above as Sampling Method 5. Inexpensive test papers, sensitive to various elements are manufactured by Macherey, Nägel and Co. (D-516 Düren, P.O. Box 307, Germany). Two in particular were impressive; one is responsive to lead (Pb^{0} and Pb^{2+}) and is available under the name Plumbtesmo, and the other, called Cuprotesmo, detects copper (Cu^{0}, Cu^{+} and Cu^{2+}). For the identification, a paper of any desired size is soaked in distilled water and applied to the surface. The colour reaction appears on the paper within minutes, and the test leaves no mark whatsoever, even on a patinated surface. They are also very sensitive: 0.05μg of metal on surfaces or 5 parts per million in solution. These two test papers are the only ones which respond to metallic (non-ionized) elements. A whole range of test papers are available for other metals but some ionization must occur at the surface.

The second modification to these tests is designed to facilitate this ionization. Listed as Method 6 above,

it consists of applying a small voltage across the metal object, electrolytically removing a small sample onto a piece of moistened filter paper or test paper for identification. A diagram of one possible configuration of this method is shown in Figure 1.

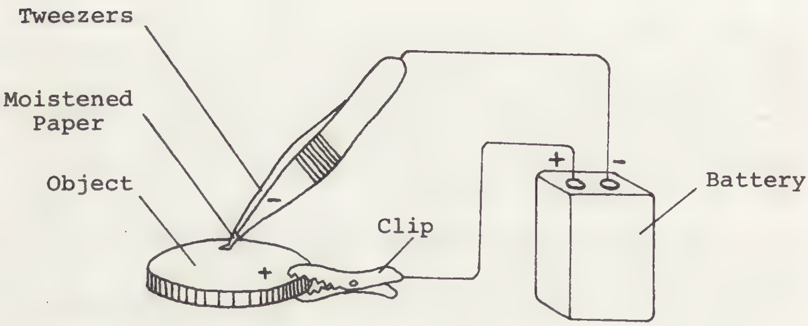

Figure 1. The electrolysis apparatus

Effects of this sampling method on metal surfaces differ considerably. For example, electrolysis using a saturated NaCl solution on a small piece (about 1 mm x 5 mm) of filter paper for 15 seconds can have the following effects: Ag is darkened, some Cu patinas are untouched while a relatively new Cu surface will be lightened ("cleaned"), Pb may be darkened, brass (if new) may be slightly darkened while old brass changes little, pure Au is unchanged, Au/Cu alloys can darken and new Fe is blackened while stainless steel darkens slightly. In most of the cases where corrosion products are present, the colour reaction on the spot test paper takes place so quickly that much less electrolysis time is required, and consequently the effects on the object can be kept to a minimum.

One great advantage of this method of sampling is the ability to precisely control the size of the area sampled on the object's surface. This area can be made extremely small merely by cutting the filter paper into a shape with a long point and placing only the end of this in contact with the object. The possibility of a drop of acid or base spreading across the surface has thus been eliminated. Porous corroded layers are not penetrated by corrosive agents but are merely wetted at

the point of contact of the filter paper. In addition, weaker solutions are often sufficient for this process to occur, as the main driving force is electrolytic.

Another advantage of using the prepared test papers and the electrolytic sample collection technique is that each replaces several liquid reagents. This not only makes the tests simpler to prepare for and to perform, but also increases their portability, should they be required by a conservator in the field.

Therefore, using a combination of the inexpensive, easily obtained test papers, the electrolysis apparatus described above, and some of the tests already listed, a revised set of spot tests has been derived. These are described in the following section.

<u>List of Recommended Spot Tests</u>

Gold (Au)
<u>Procedure</u>: Dip a small piece ($\sim 1\ mm^2$) of plain filter paper in NaCl (saturated solution in water). Electrolyze for < 15 sec.; some darkening will probably be evident if Cu is present. Leave the paper on the spot until slightly dried out so that Au is well into the paper. Dip into a $SnCl_2$/HCl mixture (20% $SnCl_2$ in 15% HCl).
<u>Results</u>: Au causes a black colour immediately, with no interference from Cu or Ag.

Copper (Cu)
<u>Procedure</u>: Wet a small piece of Cuprotesmo test paper with distilled water and place on surface.
<u>Results</u>: Cu metal or Cu^+ and Cu^{2+} ions cause the pale yellow paper to turn pink/purple. This test works particularly well on corroded or patinated areas and leaves no trace of the test. On highly polished or new surfaces the reaction is much slower and may be speeded up by a brief (about 5 sec.) application of the electrode to the test paper in order to aid the dissolution process. The cathode is placed in contact only with the wet filter paper and the anode is touched to the object at least several millimetres away.

Silver (Ag)
<u>Procedure</u>: Wet a small triangular piece of plain filter paper with 10% H_2CrO_4 and hold this in tweezers attached electrically to the cathode, and touch one of the points of the triangle to the metal in as small an area as possible for 1 second or less.
<u>Results</u>: The area of the metal touched is blackened somewhat, and the presence of Ag is indicated by red Ag_2CrO_4 in the spot.

Iron (Fe)
Procedure: For corroded objects, dip a small square of dipyridyl test paper in distilled water and place on the surface of the object. This test leaves no visible effects on the object.

Procedure: For uncorroded objects, dip a long, thin piece of dipyridyl test paper in NaCl (saturated solution) so that the paper is quite wet. Next, electrolyze with the cathode not closer than 5 mm to the object. This can be achieved by holding the test paper (about 5 mm x 1 mm) at one end in tweezers attached to the cathode, while touching the other end to a spot on the object.
Results: For both corroded and uncorroded objects, a red colour will appear on the white test paper touching the object after several seconds, if iron is present. Occasionally, the red indicator colour will appear if the first piece of test paper is removed and a dry piece is applied to the drop of liquid left on the surface of the object.

Lead (Pb)
Procedure: Wet a small square (as small as 1 mm^2) of Plumbtesmo test paper with distilled water and place on the surface of the object.
Results: The presence of Pb is indicated by a pink/purple colour, and the process has no visible effect on the surface of the object.

Tin (Sn)
Procedure: Dip a small piece of filter paper in a saturated cacotheline solution ($\sim$ 0.6%, aqueous). When the cacotheline dries slightly, dip the filter paper in NaCl (saturated solution). Hold one end of the filter paper in tweezers connected to the cathode, and touch the paper to the surface of the object.
Results: A purple colour indicates Sn. Shiny surfaces will become matte after 1 sec. of electrolysis, and be darkened slightly after 2 sec.

Zinc (Zn)
Procedure: Dip a small piece of filter paper in NaOH (5-10%) and apply all or part of the paper to the surface of the object for 5 - 10 sec. Place this paper on the corner of a large filter paper, making 2 or 3 wet spots. Wash these spots with successive drops of dithizone/CCl_4 (sat'd < 0.01% by weight in CCl_4).
Results: Pink (not orange) around the spot edges denotes Zn. Any NaOH remaining on the metal of the object should be wiped off immediately; this can be done with the same filter paper on which the dithizone reaction is to be done. In general, the test can be

done with little surface effect on the metal except that a shiny Zn surface may be slightly darkened or dulled in the area of the spot. There is a small effect on some Cu corrosion products, and a Pb surface tends to develop a shiny spot where the NaOH droplet was.

Nickel (Ni)
Procedure: Dip a small piece of Ni test paper into a saturated solution of NaCl. Apply the electrodes of the small battery so that electrolysis occurs for about 5 seconds.
Results: On drying the following colours may be observed: pink-red for Ni, brown for Fe, green for Cu and yellow for Au.

Antimony (Sb)
Procedure: Dip a small square of the Sb test paper in dilute HCl and apply this to the object.
Results: The presence of Sb is indicated by an orange colour. The reaction is complete in 5 seconds on pure Sb using 2% HCl. Surfaces containing trace Sb will be much slower. Au and Ag surfaces remain unaffected by the test, Pb is slightly darkened, Cu and Fe corrosion products change colour slightly.

Table 1. Conventional Microchemical Tests for Metals and Alloys

ELEMENT	DROP APPLIED TO OBJECT	ADD TO DROP ON OBJECT	COLLECT DROP IN PIPET CNTG:	TRANSFER TO FILTER PAPER PREV. TREATED WITH:	TREAT SPOT WITH:	FINAL COLOUR
Au (Gold)	Aqua regia conc.	-	1-2 drops NaCl(5%)	p-Dimethylaminobenzylidenerhodanine (dried)	1-2 drops NaOH(10%)	black, dk.violet =Au (blue = Cu)
Cu (Copper)	HNO_3 dil. (10%)	-	1-2 drops NaCl (5%)if Ag pres.	-	a)NH_4OH, then b)Rubeanic acid	a)blue = Cu b)green,black=Cu
Ag (Silver)	H_2SO_4 (50%)	1 drop 10% H_2CrO_4	-	-	-	red crystals of Ag_2CrO_4= Ag
Fe (Iron)	HNO_3 dil. (10%)	-	-	-	a)$K_4Fe(CN)_6$ or b)NH_4OH fumes	a) blue = Fe b) brown = Fe
Ni (Nickel)	HNO_3 conc (70%)	-	-	-	NH_4OH to neut., 1 drop CH_3COOH then 1 drop Dimethylglyoxime	pink/red spot=Ni
Pb (Lead)	CH_3COOH (35%)	1 drop 10% H_2CrO_4	-	-	-	yellow ppte of $PbCrO_4$= Pb
Sn (Tin)	HCl (20%)	-	-	Cacotheline (still damp)	-	perm.purple = Sn fugit.purple =Cu
Zn (Zinc)	NaOH (10%)	-	-	-	several drops dithizone at centre of spot (CCl_4 evap'd after drops)	both pink within & near edges of orig. spot and pink halo,extends into dithizone
Sb (Antimony)	HCl (20%)	crystal of $NaNO_2$	-	Rhodamine B (dried)	-	purple = Sb

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Appendix 1. List of Reagents

a) The following is the complete description of reagents listed in Table 1 for the conventional spot tests given.

Acids and Bases: the strength of all acids and bases is given on the table in % by weight in aqueous solution (i.e. CH_3COOH (35%)).
aqua regia......1 vol. HNO_3(conc): 3 vols HCl (conc).
NaCl............5% by weight, aqueous
$K_4Fe(CN)_6$.......5% by weight, aqueous
$NaNO_2$...........crystals

p-Dimethylaminobenzylidenerhodanine.......saturated ∿0.05%, in ethanol
Rubeanic acid (dithio-oxamide)...........saturated, ∿1% in ethanol
Cacotheline (nitrobruciquinone hydrate....saturated, ∿0.06% aqueous
Dimethlglyoxime (diacetyldioxime).........1% in ethanol
Dithizone (diphenylthiocarbazone).........saturated, <0.01% by weight in CCl_4
Rhodamine B (tetraethylrhodamine).........0.01% aqueous solution

Other Equipment:

Whatman #5 Filter Paper
disposable pipets

b) The reagents and test papers needed to perform the improved tests recommended in the text are listed below.

NaCl..........saturated, aqueous
NaOH..........5-10% by weight, aqueous
H_2CrO_4........10% by weight, aqueous
HCl dil.......2-5% by weight, aqueous
$SnCl_2$/HCl.....$SnCl_2$ 20% by weight in HCl 15% by wt.

Cacotheline (nitrobruciquinone hydrate)...saturated, ∿0.6% aqueous
Dithizone (diphenylthiocarbazone)........saturated, <0.01% by weight in CCl_4

Test Papers (Macherey, Nägel and Co., D-516 Düren, Germany, P.O. Box 307):

Cuprotesmo
Plumbtesmo
Dipyridyl test paper

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Nickel Test Paper
Antimony Test Paper

Other Equipment:

Whatman #5 Filter paper
disposable pipets
9 v. battery, connecting wires and clips, a 280Ω resistor (limits current to 25 ma), metallic (conducting) tweezers

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12. Spot Test Papers are available from Macherey, Nägel and Co., D-516 Düren, P.O. Box 307, Germany.

13. Koslow Spot Kits, Koslow Scientific Co. Ltd., 7800 River Road, North Bergen, New Jersey, U.S.A. 07047.

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CORROSION INHIBITORS

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CORROSION INHIBITORS

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ABSTRACT

Information with respect to inhibitors of metal corrosion, which is thought to be relevant to museum curators, restorers and collectors, is reviewed. Inhibitors of inorganic nature are mentioned, awhile organic inhibitors, because of their multiplicity and importance, are dealt with extensively. A special attention is bestowed on the Vapour Phase Inhibitors, and their use in closed spaces, such as glass-cases and depots, is emphasized. The health hazards involved in working with those chemicals are also discussed.

Restriction of metal corrosion is partially or entirely attained by the use of inhibitors which may be organic or inorganic compounds or a mixture of both. The mechanism of inhibition involves various types of screening, the principle purpose of which is to sever the material exchange between metal and environment, and thus to prevent the origination or the further growth of corrosion layers on the metal. Inhibition is particularly important when corroded metal objects are being cleaned by means of acidic solutions, although a similar need of inhibitor, but of a different composition, is also essential for metals like copper, lead and tin, when immersed in alkaline cleaners. Another application of the inhibitors is procured by the capability of some of them to seal the porous corrosion film on a metal, turning it, accordingly, into a protective layer. In addition, an inhibitor may also play a distinctive role in the protection of metals that are kept in closed spaces.

Inorganic salts as sodium nitrite, sodium chromate and sodium bichromate are good corrosion inhibitors for metals immersed in fresh water that contains practically no salts, but also in brine and in seewater - hence they are commonly added to the water that is used to rinse cleaned metal objects in restoration workshops.
The majority of inhibitors are, however, of organic nature. Of these, both natural and synthetic compounds are used as inhibitors. The natural compounds include: low-grade flour, gelatin, glue, sludge from petroleum, animal wastes, sulphonated coal-tar products, asphaltum and wood tars. Synthetic inhibitors are, however, more effective as they may be designed to serve any particular purpose with respect to the metal undergoing treatment, and, are therefore increasingly and in a great many varieties being produced. They comprise: nitrogenbase materials and their derivatives, pyridines, quinidines, aldehydes and also thioaldehydes as well as many other sulfur-containing products. Compilation of these compounds is the theme of many studies/2, 16, 12, 3/, and if selection of a synthetic inhibitor from the checklists enclosed therein is intended, it should be done after considering the following factors/ 9, 15/ :

- Compared to aliphatic amines, the aromatic amines are inferior inhibitors. Saturation of the aromatic or heterocyclic ring improves the inhibition.
- Sulfur-containing organic compounds are superior inhibitors to the amines.
- Concentrations ranging from 0.5% to 1% of inhibitor are in most cases sufficient. But inhibitor concentrations that protect for 24 hours will not necessarily do so over longer periods.
- The concentrations of inhibitors required for protection are little affected by temperature up to 70°C, but higher concentrations of inhibitors are required above this temperature.
- The concentration of aggresive ions (Cl^-, SO_4^{2-} or NO_3^-) capable of causing failure of inhibition is related to the inhibitor concentration; the valency of the aggresive ion being the decisive element in this relation, i.e. in the presence of chloride lower concentrations of an inhibitor are required than would be the case with sulfate present.

In order to prevent attack on the metal proper, corroded copper and its alloys are stripped in acid baths to which an inhibitor (thiourea or gelatin) is added. For alkaline corrosion cleaners, however, either β-naphtol or furfurol is recommended.

Rusted iron objects are effectively cleaned in acid rust-removers that contain sufficient amount of any of the already mentioned organic inhibitors. On the other hand, derusting of iron in alkaline fluids does not require an inhibitor.

Sealing of the corrosion crust on copper and its alloys by means of 3% solution of benzotriazole in alcohol with the intention of assuring protection has been carried out by BLECK/1/. From his experiments he was able to draw the conclusion that benzotriazole reacts both with univalent and bivalent copper salts and forms with them polymeric compounds of fibrous structure that are insoluble in water and resistant to temperatures well up to 200°C. The continuous decay of malignant patina may, due to this property of benzotriazole, be effectively arrested. Severely chloride-infested patinas require for such stabilization of course, repeated treatments with higher concentrated alcoholic solutions of benzotriazole.

The vapour phase inhibitors (V.P.I.) are compounds that display a tendency to protect metals by their vapour. They are therefore suitable for use in museum glass-cases and during storage. The general conception as to the action of these inhibitors implies that by being adsorbed on metals, a V.P.I. manages to displace water already present and that thereafter the metallic surface keeps hydrofobic. It also fixes the pH-value at the interface metal/air so that the resulting pH will not favour attack on the metal. And finally, the V.P.I. is chemisorbed on the metals, creating thus a protective barrier.
The organic products of effective vapour phase inhibiting performance may be classified as follows/6/ :

- Nitrite of diisopropylamine, nitrite of diisobutylamine, nitrite of dicyclohexylamine.
- Carbonate of dicyclohexylamine, carbonate of monoethylamine.
- Benzoate of amylamine, benzoate of isopropylamine, benzoate of ethanolamine.

It appears that the presence of certain radicals in the chemical formula of the V.P.I. determines the protective propensity. Hence ferrous metals and alloys are best protected with compounds containing a nitrogroup, whereas in the case of copper and its alloys, in order to attain a similar protection, chemicals containing a carboxyl group are required. Besides, V.P.I. perform better when they evaporate from a carrier. Some claim that the best carrier is anti-corrosion grease/5/, but paper and also textile, foam, etc./10/ impregnated with V.P.I. is reported/6/ to be just as effective. The worst performance is observed when the V.P.I. are used as powder, in sachets or in tablets/5/. Practically significant with respect to protection of metals is that dicyclohexylamine nitrite and cyclohexylamine carbonate are the two most recommended V.P.I. for iron and steel (60 parts of V.P.I. and 21 parts of casein are mixed with 120 parts of water and the mixture is applied on paper, textile fabrics, foam, etc.).

Dicyclohexylamine nitrite is also a good protector for copper and its alloys. Cyclohexylamine carbonate on the contrary accelerates their corrsosion/15/. Other inhibitors, such as morpholine, methylmorpholine, ethylene diamine and propylene diamine used alone (or

mixed with another substance which can sublime) prevent satisfactorily the atmospheric corrosion of alloys containing copper. Yet, in this group of inhibitors pyridine, quinoline, β-picoline, phenol and monoethanolamine must be included. Paper impregnated with 0.5-1% benzotriazole is also reported to serve as a V.P.I. for these metals /3/.

A V.P.I. of chemical composition similar to the nitrite salt of dicyclohexylamine is recently described as a reliable means to protect silverware and to prevent tarnishing discoloration on it/10/. An additional advantage of this new product stems from the fact that the inhibitor is incorporated in a foam block provided with an adhesive strip so that it can be attached to any surface, but is at the same time almost unnoticable and does not interfere disapprovingly with the appearance of the silverware (Silver Safe Tarnish Inhibitor. Supplier: Singer Products Company Incorporated, One World Trade Center, Suite 2365, New York, N.Y. 10048, U.S.A.).

Chlorophyll is also an excellent V.P.I. for silver.
An essential requisite for the avoidance of tarnishing through its employment is that the silver object must be laid in exhibition glass-cases on a fabric of cellulosic nature such as tissue paper, cotton, flaxen jute, etc. (but by no means on woollen fabrics) that have been impregnated prior to use, with chlorophyll. The impregnation is carried out with 5% solution of oil-soluble chlorophyll dissolved in white spirit. The impregnation should be repeated until about 5% chlorophyll by weight has been absorbed by the cellulosic material, which is only then worthy as a V.P.I.. After drying the material is ready for use as anti-tarnishing agent.

The corrosion inhibitors offer undoubtedly quite attractive advantages to museum curators and collectors. It is true that they protect metal objects, but they are at the same time confirmedly harmful to human health and, because of this, are commonly indicated in chemical hazard manuals as the initiators of various occupational diseases. Sensible practitioners who intend to employ them should, in their own interest, first study the risks these chemicals involve.

Chromates and bichromates cause "chrome ulcers" or "holes" in the skin as well as dermatitis. Inhalation of vapour from their solution leads eventually to lungcancer. There may, however, be a delay of up to 30 years before any symptoms of carcinoma appear - a possible prolongation of the incubation-period that is actually characteristic for all varieties of occupational cancer/8/.

The amines, generally, are irritant to the eyes, the nose and the throat. The also irritate or burn the skin and interfere with the nervous system. But more than that, the aromatic amines are suspected to be carcinogenic/7/. Furthermore, the cyclic amines, like cyclohexylamine carbonate, are similarly suspected of being both carcinogenic and mutagenic chemicals and hence are considered to be even more harmful than many other amines/4/. The very considerable toxicity of the commonly used V.P.I. as cyclohexylamine carbonate and dicyclohexylamine nitrite are quite elaborately discussed by PAUSTOVSKAYA/13/.

There seems to be sufficient reason for much precaution when benzotriazole is used as an inhibitor/11/. The suspicion that it is also a carcinogen becomes substantial when benzotriazole is submitted to structural comparison with respect to the already recognized carcinogenic aromatic amines; the more so as here again the long-term-incubation of occupational cancer should be taken into account and a warning that it might appear later on is, to say the least, an obligation to those who promulgate the merits of benzotriazole. In addition, benzotriazole is capable of deteriorating the connective tissue of the liver/1/.

Finally, the V.P.I. based on organic sulfur compounds are known both as irritants of the skin, respiratory tract, the mucous membranes and as depressants of the central nervous system/14/.

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78/23/10

CLEANING AND CONSERVATION OF ARCHAEOLOGICAL OBJECTS MADE OF COPPER AND ITS ALLOYS

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CLEANING AND CONSERVATION OF ARCHEAOLOGICAL OBJECTS MADE OF COPPER AND ITS ALLOYS

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In the last few years in the Soviet Union archaeological excavations have been carried out on a large scale. This is due to intensive studies of historical and archaeological monuments - the circumstance which in its turn entails further growth of the restoration work, in particular the cleaning and restoration of metals - copper and its alloys.

A rapid and reliable method for the cleaning and conservation of archaeological objects made of copper and its alloys has been worked out in the chemical restoration laboratory of the Georgian Museum.

The essence of the method consists in dissolution of corrosion products and in electrochemical restoration of metal with subsequent conservation. Prior to passing to the description of the method it is appropriate to mention briefly the work that preceded the creation of the method.

As a result of long chemical and technological research it was established that objects made of pure copper are a rarity. At the beginning of the IV - III millennium archaeological objects are represented by arsenical copper with a rather low content of ore elements. It is rarely that the content of arsenic and other admixtures exceeds 5%.

In the II millennium B.C. the content of alloying elements goes up to 15% and is represented mostly by tin, while the I millennium A.D. is marked by the existence of complex alloys with a high content of alloying elements, in most cases exceeding 30%. These latter are represented by tin, lead and zinc.

Though metallic objects of different dates vary in their chemical composition, the products of corrosion are represented mostly by copper compounds. These are of different composition and nature: they are represented in the form of carbonates or in the form of chlorides and oxides or - which is the most frequent case - in the form of a combination of all three.

It is known that in the course of a long corrosive process the isolation of one of the component phases is intensified by its active oxidation. As the corrosive process progresses the most active component is oxidized, while the rest remain unchanged. In the case of corrosion of copper and its alloys the oxidation process is quite

similar. Copper is a more active metal in comparison with tin; therefore it is mostly copper that undergoes oxidation.

Our cleaning method is based on dissolving corrosion products in such a way that the solvent would not affect the non-oxidized metal.

Cuprous compounds were dissolved by 3-5% sulphuric acid solution. The duration of dissolving depends on the thickness and qualitative composition of the corrosion layer. Carbonic and oxide compounds are completely dissolved by the sulphuric acid. From time to time the object is taken out of the acidic solution and is washed with water and a soft brush. The object remains in the solution till the corrosion products are completely removed. Then one proceeds to electrochemical restoration by atomic hydrogen.

In the process of cleaning under the carbonate layer one often finds cuprous monochloride which is not acted upon by the sulphuric acid. In that case the object should be treated with potassium hydrate solution of a high concentration. Very often corrosion layers of cuprous monochloride and of other oxide compounds alternate with one another. In that case treatment with the sulphuric acid and potassium hydrate should be accordingly alternated, till the corrosion layers are completely dissolved. Only after that may the object be treated with zinc.

The object to be restored is subjected to the action of atomic hydrogen.

Hydrogen is, as known, a deoxidizing agent. Its deoxidizing properties sharply increase in the atomic condition. In the atomic condition hydrogen stays for a very short time (for a hundredth fraction of a second), i.e. directly at the moment of isolation. When subjecting the object to the action of atomic hydrogen, the treatment must be conducted in the place where hydrogen is obtained. This is easily feasible, if the object is covered over with granulated zinc and is thereafter treated with diluted sulphuric acid.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$$

After the hydrogen isolation reaction stops, small portions of concentrated sulphuric acid are added to the vessel with zinc.

In the case of an intensive treatment with atomic hydrogen the electrochemical restoration process lasts for 4-5 hours. This time is sufficient for the corrosion products that remain in the pores to dissolve.

$$CuO + 2H \longrightarrow Cu + H_2O$$

$$Cu_2O + 2H \longrightarrow 2Cu + H_2O$$

The object is then removed from zinc, washed with running water and kept in distilled water for 48 hours. The water must be repeatedly changed. After water leaching (mainly of zinc sulphate) the object is transferred to the drying cabinet, where it stays for 3-4 hours at a temperature of 120-125 C.

The object - rubbed dry and clean - is immersed into hot neutral paraffin wax and is kept there till bubbles cease to appear. After that, excessive paraffin is removed with thin paper and the object is ready for long-term storage.

The above-described method was applied to the objects that had a metallic core. Otherwise treatment with the method in question is not expedient.

The method allows simultaneous treatment of hundreds of objects, makes additional mechanical cleaning unnecessary and guarantees after conservation long-term storage of the object.

The number of objects thus treated amounts to 15,000. They have been kept under observation for over two decades. It may be said with certainty that not a single case of repeated corrosion has been registered during the observation period.

78/23/11

L'APPORT DE LA SPECTROMETRIE D'EMISSION A PLASMA DANS L'ANALYSE DES OBJETS METALLIQUES ANCIENS

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Zagreb, 1978

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Depuis plusieurs décennies, la spectrographie d'émission dans l'ultra-violet a constitué l'une des techniques privilégiées pour l'analyse élémentaire des métaux anciens, tout particulièrement dans le cas de l'étude de séries importantes d'objets.

Toutefois, certains problèmes techniques n'étaient pas entièrement résolus, les uns inhérents à la méthode elle-même, d'autres étant liés à son application aux objets d'art.

Des analyses comparatives conduites sur des matériaux archéologiques (ICOM 1972) ont mis en évidence ces problèmes dans la mesure où l'utilisation de techniques différentes aboutissaient parfois à des résultats différents, particulièrement pour les éléments traces.

La mise au point de nouvelles sources d'excitation à plasma ayant permis de résoudre les principaux problèmes techniques (étalonnage, effets de tiers-élément et de matrice), de nouvelles possibilités s'offrent pour l'analyse des matériaux archéologiques :
- analyse d'un élément quelconque y compris les éléments majeurs dans les alliages les plus divers sans préparation d'étalons solides.
- analyse des échantillons non conducteurs : corrosions et surtout minerais et scories dont l'étude est importante dans la recherche de l'origine des objets.
- normalisation des conditions opératoires facilitées par le fait que l'étalonnage et les dosages sont réalisés sur solution.

Le rapport présenté au congrès de l'ICOM de 1972 concernant une étude sur l'analyse comparative interlaboratoire d'objets en bronze a montré dans quelles limites pouvaient varier les résultats obtenus sur un même échantillon lorsque différentes techniques d'analyse élémentaire étaient employées par plusieurs laboratoires.

Les écarts relatifs observés étaient souvent de l'ordre de 50 p.cent et pouvaient atteindre 300 à 400 p.cent pour les faibles teneurs.

Il a également été montré que l'homogénéité des résultats variait selon la technique utilisée et que c'est l'analyse par absorption atomique qui s'est révélée la meilleure à cet égard.

L'explication de ces résultats parfois très divergents nous paraît résider dans le mauvais contrôle de certains paramètres intervenant dans le processus analytique . Parmi ceux-ci, les plus importants sont :

- la stabilité du phénomène mesuré
- l'étalonnage
- les effets de matrice et de tiers-élément.

En conséquence, une méthode analytique peut être considérée comme d'autant plus fiable qu'elle maitrise mieux ces paramètres.

Or, deux de ces paramètres au moins posent des problèmes qui sont généralement incomplètement résolus :

- <u>l'étalonnage</u>

Nous savons, pour l'avoir expérimenté, que l'élaboration d'étalons solides d'alliages métalliques présentant de bonnes qualités d'homogénéité se révèle pratiquement irréalisable.

- <u>les effets de matrice et de tiers-élément</u>

La correction de ces effets est souvent négligée parce que trop complexe. Elle nécessite en effet la parfaite connaissance de la nature du matériau analysé ce qui n'est généralement pas le cas, faute du temps ou de l'équipement nécessaire. Ainsi, par exemple, le degré de corrosion d'un échantillon métallique est-il souvent difficile à apprécier par un simple examen visuel.

Les corrections à effectuer sont encore plus difficiles lorsqu'il s'agit d'analyser des matériaux complexes et de compositions très variables tels que les minerais, les corrosions ou les scories ; pour ces matériaux, le problème de l'étalonnage se pose alors de nouveau d'une manière plus aigue encore.

La spectrométrie d'émission à plasma que nous utilisons au Laboratoire de Recherche des Musées de France (et qui équipe également d'autres laboratoires tel que celui du Smithsonian Institute de Washington) présente les principaux avantages suivants :

- très bonne reproductibilité des mesures (l'écart-type relatif peut être inférieur à un pour cent)
- suppression du problème de la normalisation de l'étalonnage. En effet, les étalons étant eux-mêmes sous forme de solution ne posent pas de problèmes d'hétérogénéité et peuvent être fabriqués par chaque laboratoire.
- Diminution considérable des effets de matrice et de tiers-éléments en raison de la très haute température à laquelle se trouve porté l'échantillon et de son état très dilué sous forme d'aérosol. Ces effets ne sont plus sensibles qu'aux très faibles teneurs et sont pratiquement négligeables dans la gamme des concentrations usuelles.

L'analyse de matériaux très divers, tels que corrosions, minerais ou scories peut ainsi être effectuée sans correction d'effet de matrice.

- Possibilité d'analyser par une seule technique,

les éléments majeurs (dont la matrice), mineurs et traces. En effet, la distinction traditionnelle entre ces éléments n'a plus de sens, du point de vue analytique, puisque l'on peut, par dilution, se ramener à la gamme de teneurs optimale désirée.

- un élément quelconque peut être analysé puisqu'il suffit pour cela d'acquérir ou de préparer la solution étalon correspondante.

Plusieurs centaines d'analyses ont ainsi été effectuées par spectrométrie d'émission à plasma au Laboratoire de Recherche des Musées de France.

Parmi les problèmes abordés, citons :

- l'analyse d'objets byzantins en argent dans lesquels nous avons pu doser des éléments qui ne sont généralement pas analysés en raison de l'absence d'étalons : l'étain, le zinc, le bismuth.
- l'analyse, en collaboration avec le Commissariat à l'Energie Atomique, de minerais de cuivre iraniens, pour une étude des corrélations objets-minerais.
- l'étude comparative métal-corrosion sur des objets en cuivre appartenant au Département des Antiquités Orientales du musée du Louvre.

En conclusion, il nous semble que l'application de la spectrométrie d'émission à plasma à l'analyse des objets métalliques anciens doit permettre de résoudre les problèmes de normalisation des conditions expérimentales.

En conséquence, l'utilisation réciproque des résultats analytiques obtenus dans différents laboratoires utilisant cette technique nous paraît dès maintenant réalisable et rend possible une large collaboration interlaboratoires au profit d'une connaissance plus approfondie des problèmes concernant l'origine et la technologie des objets.

78/23/11

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78/23/12

RECENT DEVELOPMENTS IN THE CONSERVATION OF OUTDOOR BRONZE MONUMENTS

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RECENT DEVELOPMENTS IN THE CONSERVATION OF OUTDOOR BRONZE MONUMENTS

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As an introduction to the work of the Center for Archaeometry project of research and practical application in the conservation of outdoor bronze monuments, views of two bronzes, before and after treatment, are here presented. The slides are of the von Humboldt and Shakespeare statues in St. Louis, both by Ferdinand von Muller, Jr., and both cast in Munich and dedicated in the 1880's. They are fairly typical examples of the eighteen large-scale sculptures that we have treated during the past year. (1 through 9)

Our work at Washington University in St. Louis began as a collaboration between Chemist and Conservator towards solving the conservation problems of a large fountain complex, and has now developed into a collaborative effort of chemist, physicist, metallurgist and conservator. Our initial studies and observations and recent studies by others such as Riederer in Berlin, Lehmann in Poland, and Panseri and Leoni in Italy, clearly demonstrate that: 1) outdoor bronze monuments in urban areas have been undergoing serious corrosive attack since industrialization, 2) the attractive natural patinas of the past have been replaced by thick, opaque and normally very heterogeneous accumulations of corrosion products and accretions, 3) the corrosion products are primarily basic copper sulfate, and 4) that these corrosion products are not protective of the metal underneath as has often been assumed. Statues in St. Louis exposed for twenty years or more have lost one millimeter or more of metal. Considering that the average large-scale bronze is approximately six to ten millimeters thick, we estimate that the average, typical loss of metal for a seventy-year-old statue is between ten and twenty percent.

In solving the problem of safely removing the very hard and well-adhered soot and calcium encrustation from the Milles fountain in St. Louis we arrived at the use of a low-pressure glass bead peening or blasting technique. (10) Glass bead peening has been in use since the 1930's in industry as a means of developing substantially increased fatique resistance through the creation of a layer of residual compressive stress on high-performance alloys of steel, aluminum and titanium. It has found important application in the aircraft industry and has been important as a means of preventing stress

corrosion. Glass bead peening provides a clean uncontaminated surface, and can be used with a great degree of control on delicate machine parts. Of all cleaning methods for bronze statues it is by far the safest as it removes practically no metal--less than a micron-even with prolonged exposure to the blast stream, and provides the beneficial effect of work-hardening the surface, thereby sealing microscopic pits and cracks and making the metal surface more resistant to corrosive attack by the atmosphere.

(11) The principal aims of our studies over the past year have been toward studying atmospheric corrosion of bronze, towards developing a methodology of documentation and technical examination for outdoor bronze sculpture, and towards exploring and refining methods and materials used in treatment. We have also worked towards an articulation of the aesthetic problems involved in the treatment of outdoor bronzes and have sought active collaboration with sculptors, founders and art-historians.

Thus far our methods of technical examination begin with extensive photographic documentation on a normal and macro scale. (12 through 14) We have devised a method of extracting a 6 mm. diameter core sample that involves first drilling a hole in the metal (15), attaching a guide plate to keep the drill in position in starting the core drill, (16) removing the guide and inserting a spatula that supports the sample and prevents its loss in the final stage of drilling.(17) Normally three holes (18) are required and are plugged with bronze plugs (19 20) wrapped with Teflon tape for a tight fit. (21) Sample scrappings are made of encrustations and corrosion products. The plugs are sectioned and studied by classic metallographic techniques, and in the scanning electron microscope with microprobe. Part of the plug is analyzed for alloy content by atomic absorption. Scrapings and corrosion products are analyzed by x-ray diffraction. We were able to make a radiograph (22) of one of the statues, the <u>George Washington</u>, using Iridium isotope as a radioactive source at a distance of about ten feet and with about one hour exposure time. An unusual degree of porosity was revealed in the metallographic study and in the radiograph, and this appears to have been a major factor in the severe deterioration (23-24) suffered by this statue, a copy of Houdon's marble unveiled in St. Louis in 1873. In this bronze and in well over half of the statues we have examined, we have observed severe intergranular attack (25) which was something we had not expected. Statues with intergranular attack appear to be those with a tin content of six to ten percent or more.

The great variety and varying degrees of corrosive attack have also been quite surprising. The oldest St. Louis bronze, the Senator Benton (26) by Harriet Hosmer dating from the 1860's, had a more generally even green appearance, though still quite disfigured in important areas (27), and it displayed corrosive attack to a far less degree than any of the other monuments treated. (28-30 and compare 30 (Benton) with 31 (Washington)) One explanation might be that it was originally exposed to the atmosphere in less polluted times, but the etched cross-section revealed a very compact <u>wrought</u> structure, and this factor appears to have been important in reducing corrosive

attack, as it has been observed that wrought copper roofs do not suffer the kind of pitting attack commonly suffered by statues made of cast metal. This phenomenon can be observed on patches (32-33) that received a greater degree of surface working than surrounding cast metal, and probably explains why severe pitting attack is less prevalent in early bronzes (34) that were commonly highly worked--this example dating from the 16th century. Another surface feature that appears to have a marked protective effect can be observed in areas that have been highly polished by frequent touching. (35) This statue (36) in St. Louis, entitled The Naked Truth, while displaying the normal severe pitting attack (37-38) in most areas, had virtually no pitting attack in the lap (39) which had received a high polish from neighborhood children who like to climb up on the statue. The amount of metal lost from abrasion by children's feet was far less than that lost by attack from atmospheric pollutants. (40) This view of the foot of D.C. French's Alma Mater at Columbia University in New York clearly shows the rubbed area standing out in relief from the pitted (unrubbed) areas adjacent.

A good example, aside from the details of pitting that have been shown, that demonstrates the severity of loss, can be found in the Shakespeare statue previously shown (41), where a liquid substance, perhaps pine sap, dripped on to the statue fairly early on and served to protect the metal in that area. (42-43) On the base of the statue (44) the area protected by the drip stands a full millimeter (45) above the tops of the surrounding pits. Needless to say, this serves to demonstrate the importance of providing outdoor bronzes with an adequate protective coating.

In conclusion, a brief comment on outdoor corrosion tests underway at five Regional Air Pollution Stations in the St. Louis area. (46-47) We are comparing two different alloys, 89-11 and 85-5-5-5 bronze, several different surface treatments and cast and wrought structures. Results after about a year of exposure show that the 85-5-5-5 alloy darkens considerably faster then the 89-11 alloy (48). The highly polished plates show the least darkening, and the peened plates (49) show no more and in some cases less darkening than unpeened samples. Areas peened at higher pressure (80 psi cf. 40 psi) and with a slightly larger bead (125 micron cf. 75 micron) appear more resistant to tarnishing than areas peened at lower pressure with smaller bead.

LIST OF SLIDES

Description by:

	Location	Artist	Title	Subject
1.	St. Louis	Von Muller, II	Von Humboldt	Full view before treatment
2.	"	"	"	Detail, head before treatment
3.	"	"	"	Fullview, after treatment
4.	"	"	"	Detail relief on base before treatment
5.	"	"	"	Detail relief on base, after treatment
6.	"	"	Shakespeare	Full view, after treatment
7.	"	"	"	Face, before treatment
8.	"	"	"	Upper torso, after treatment
9.	"	"	"	Face, before Treatment
10.	"	Carl Milles	Meeting of the Waters Fountain	Glass Bead Peening
11.	"	A. Houdon cast in bronze 1860's by Hubbard	George Washington	Full view before treatment
12.	"	"	"	Detail face, before treatment
13.	"	"	"	Proper left hand before treatment
14.	"	"	"	Detail of 13
15.	"	"	"	Coring technique, drilling 1st hole

	Location	Artist	Title	Subject
16.	"	"	"	Coring technique, attachment of template
17.	"	"	"	Coring technique, insertion of spatula
18.	Coring Technique - Holes after extraction of Core			
19.	Coring Technique - Holes plugged with Bronze Plugs			
20.	Coring Technique - The core sample Extracted			
21.	St. Louis	Houdon-Hubbard	George Washington	Sample scrapings of corrosion products and accretions
22.	"	"	"	Radiograph, Detail, proper right side of head and shoulder
23.	"	"	"	Detail, forehead, left-side cleaned showing pitted metal, right side uncleaned
24.	"	"	"	Detail eye after cleaning showing pitted metal
25.	Metallic Cross Section, George Washington, showing intergranular corrosion before etching.			
26.	St. Louis	H. Hosmer	Sen. Thomas Benton	Full view before treatment
27.	"	"	"	Detail head before treatment
28.	"	"	"	Detail head, after cleaning
29.	"	"	"	Detail, surface after cleaning
30.	"	"	"	Detail NOSE after cleaning
31.	"	Houdon-Hubbard	G. Washington	Detail NOSE after cleaning

32. St. Louis	Houdon-Hubbard	G. Washington	Detail patch, proper left elbow
33. "	McDonald	Wm. Bates	Detail, patch on shoulder
34. Florence, Italy	Benvenuto Cellini	Perseus	
35. "	"	"	Detail, Medusa's right arm showing polishing of surface
36. St. Louis	Wandscneider	The Naked Truth	General View
37. "	"	"	Detail proper left hand
38. "	"	"	Detail of 37
39. "	"	"	Detail, lap showing polishing of surface
40. New York, Columbia Univ	D. C. French	Alma Mater	Detail toes showing polished and pitted areas
41. St. Louis	Von Muller, II	Shakespeare	Detail, torso showing dark accretion, before treatment
42. "	"	"	Detail, torso, area of dark accretion, after treatment
43. "	"	"	Detail of 42
44. "	"	"	Detail of base, area of dark accretion, after cleaning and patination
45. "	"	"	Detail of 44
46 EPA/RAPS	Atmospheric Testing Station		
47. "	"		Roof Racks for Exposure Tests

48. EPA/RAPS Test Panel 89-11 alloy bronze-cast upper right-as cast, lower left polished, lower right, peened-leftside smaller bead and 40 psi, right side higher pressure 100 psi and larger bead.

49. Detail of lower right panel shown in slide 48 leftside peened with smaller bead, lower pressure (40 psi) rightside peened with larger bead, higher pressure 100 psi.

78/23/13

NOTES ON THE CONSERVATION OF IRON, ESPECIALLY ON THE HEATING TO REDNESS AND THE LITHIUM HYDROXIDE METHODS

E.W. Fabech and J. Trier

Forhistorisk Museum
Moesgard
Denmark

ICOM Committee for Conservation
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Zagreb, 1978

NOTES ON THE CONSERVATION OF IRON, ESPECIALLY ON THE HEATING TO REDNESS AND THE LITHIUM HYDROXIDE METHODS

E.W. Fabech and J. Trier

Introduction The Prehistoric Museum, Moesgard, has archaeological and anthropological collections from many parts of the world but has specialized in Danish Prehistory. Our Iron Age covers the period approx. 500 B.C. - A.D. 1000 and iron from this period is found all over the country. Thus our laboratory has to conserve a great amount of such material causing us espec ial problems.

During the seminar in Krakow* the heating-to-redness procedure and the LiOH-method were often discussed, and we have therefore decided to go further into these methods after some general remarks on the conservation of iron.

*ICOM Committee for Conservation, Working Group on Metals: The Conservation of Iron Objects found in a Salty Environment. Krakow, Poland, 4-6 October 1976

Environment There are many environmental factors which increase the corrosion of our prehistoric iron objects. Due to our geography, iron is often found in coastal regions, which the wind steadily supplies with salt water in the form of fine droplets. The extensive use of fertilizers as well as the nearness of the British and Central European industrial areas also contributes to the corrosion of iron. Most serious is undoubtedly the substantial lowering of the groundwater by 1-2 metres, with the result that in many places the objects are exposed to oxygen even deep in the soil.

Procedure At our conservation lab all the main methods of conserving iron are used. They are shown in the flow diagram, Fig. I, and in the following we will stress those steps in the treatment which are considered of special importance.

Preliminary treatment It has become increasingly common practice with important finds that we join forces with the archaeologists during excavation, first cleaning the objects and then storing them in a protective millieu. Iron objects are usually placed in sodium sesquicarbonate solution and preferably in a cool place to avoid accelerated corrosion.

PROCEDURES IN THE

CONSERVATION OF IRON

at
the Conservation Dept.
Prehistoric Museum,
Moesgard, Denmark.

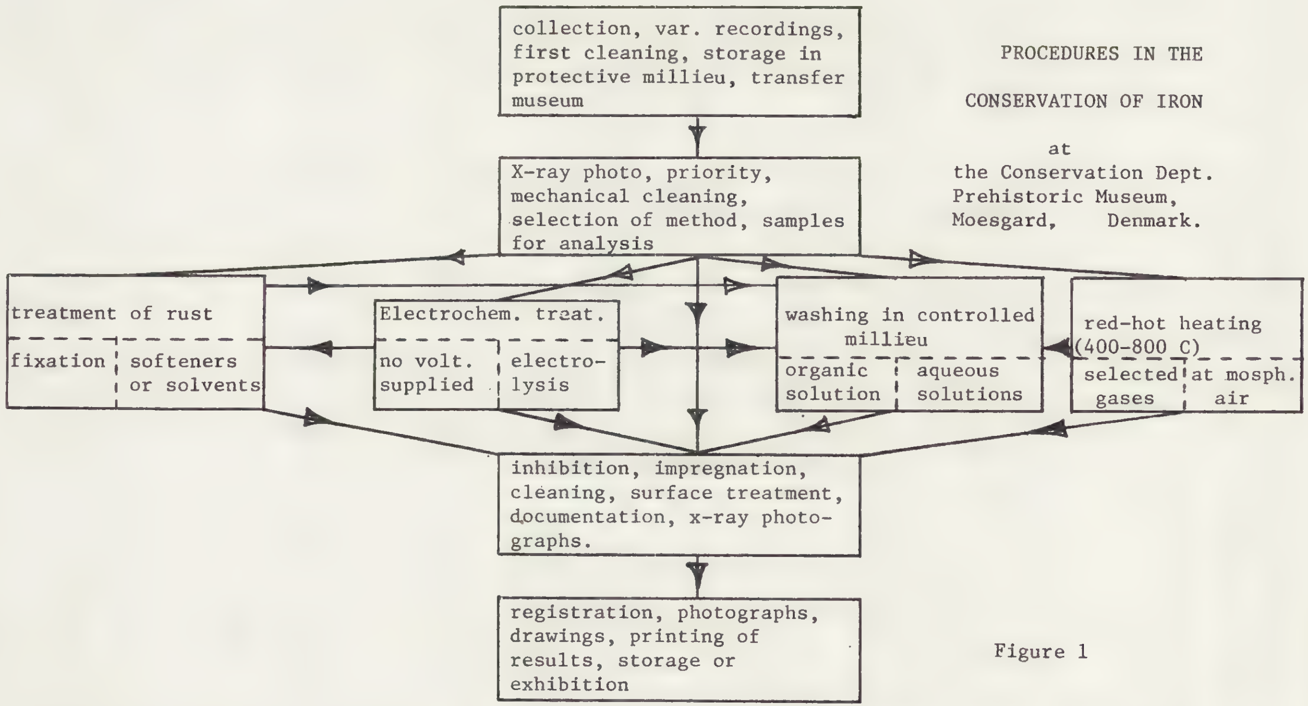

Figure 1

Shortly after arrival at the conservation laboratory all iron is X-radiographed and thereafter placed in the cooler (at about 5 C), until conservation can be undertaken. Usually many procedures are now available, but they all have their advantages or disadvantages with regard to efficiency, cost, length of treatment, final surface etc.

Conservation We have divided the procedures into four principally different methods, each again divided into two submethods. As seen in the flow diagram the methods may be combined.

1. Rust treatment, where either the rust is stabilized (e.g. using tannic or phosphoric acid) or/and loosened by using softeners (e.g. penetrating oils) or solvents (oxalic acid, citric acid, etc.).

2. Electrochemical treatment, without using external voltage supply (usually called electrochemical reduction) or electrolysis.

The procedures under these two main methods (1 or 2) are so varied and often referred to, that no more needs to be said here.

3. Washing in aque ous or organic solutions (with or without electrolytic precipitation of washed-out ions). As seen in the diagram most conservation processes are followed by washing, which however, very often is not continued long enough, perhaps because it is difficult to measure the remaining but still harmful residues of salts.

4. Heating to redness in gases, either the atmosphere or a selected mixture of inactive and/or reducing gases (N.B.: when using this method it is important to take samples of the metal prior to the treatment, because structural changes cannot be avoided).

After Treatment The objects are finally inhibited and/or impregnated, mechanically cleaned, and receive a last surface treatment. It is our experience that proper impregnation is very important using at least vacuum or preferably high vacuum (10^{-4} torr at least).

After leaving the conservation laboratory the objects should still be under its care and responsibility. Particularly with regard to exhibition and storage we are working in our museum as well as on a national basis to find some realistic - that is to say economical - solutions to the problem of finding suitable air conditioning.

THE HEATING TO REDNESS METHOD

Introduction When all, or nearly all, metal of a formerly iron object has corroded, but the item is still recognisable, the method of heating to redness should especially be considered. This method of conservation is well known to Danish conservators. It was developed and described for the first time by G.A. Rosenberg in his book "Antiquités en fer et en bronze, leur transformation dans la terre contenant de l'acide carbonique et des chlorures, et leur conservation", Copenhagen 1917.

Many conservators, however, consider this method outdated and obsolete, no doubt because they have not consulted this very well documented publication based on many meticulous experiments. Rosenberg describes very closely the character of the iron, both before and after conservation, and also considers carefully when to apply the method. We think it worthwhile to reconsider the method and the literature available (see e.g. B.B. Christensen "Obsolete method of iron conservation?" Archaeologica Lundensia, pp. 299-301, 1968).

The method as practised in our lab. The objects are first x-rayed, which helps to identify and approximately date them. These photographs are especially valuable, when at the end of the conservation process one has to reveal the original surface through wax and the corrosion crust.

After mechanical cleaning, where soil and some of the corrosion, including blisters, is removed, the unavoidable breaks are joined. Then each object is wrapped in asbestos paper, which has been moistened with alcohol (not water). Very pure iron wire, about 0.3 mm in diameter, is wrapped around the paper with each winding spaced 2-3 mm apart. It is important that paper and wire fit closely to the object. Fragile or broken parts are reinforced with longitudinally placed iron wire (2-3 mm diameter) and they are again wrapped with the thin iron wire. Each object is identified by tying a thick, numbered iron tag to the object.

If a considerable number is to be treated it is advisable to bind some of the objects together or to place them in iron baskets in order to avoid mechanical damage. Before heating the objects are, if considered necessary, first soaked in alcohol and then dried under vacuum.

The heating to redness in our laboratory takes place in an ordinary ceramic oven and the temperature is raised to 800 C for one hour or more. The method may be improved by using an oven supplied with inactive or reducing gases. During the heating the water bound in the corrosion products is set free, and they are transformed into iron oxides etc. The chlorides and sulphides are disintegrated and partly set free.

The objects are now lowered while still red hot into a saturated solution of potassium carbonate in water, where they remain for about 24 hours at 100 C. The container should be well covered.

Thereafter the objects are placed in an automatic steeping device, where water is changed every 24 hours and with facilities for heating and cooling. Chloride content and conductivity are determined, and the process is continued until no change can be detected for a long period. (Alternatively the washing out of salts may be effectuated using the Lithium hydroxide - see below).

The objects are then placed on solid microcrystalline wax in the vacuum chamber, which is then evacuated. When the proper vacuum (about 10^{-4} torr) has been maintained for some time, the temperature is raised, and the objects sink into the melted wax. This prevents them from absorbing water from the atmosphere at the time when they are most hygroscopic.

The impregnation with wax is continued at a temperature up to 100-110 C. until small bubbles from the objects cease, the vacuum being continued for at least 24 hours. At the end the temperature is reduced to about 80 C., depending on the size and nature of the objects.

Finally they are placed on nets to cool; and now the iron wire, asbestos paper and wax, together with the remaining corrosion products, are removed by grinding, cutting and air-abrasion, making ample use of the X-ray photos. This step requires much practice and a sure hand.

In spite of the fact that this method has been used for many years, we believe that it can be improved in various ways, especailly by using reducing or inactive gases.

THE LITHIUM HYDROXIDE METHOD

Introduction About two years ago the so-called Lithium hydroxide method was taken into use in our lab., and it has proved very rewarding indeed. Here the salts are removed by using LiOH in pure alcohol, to which is added an accelerator. The method is based on the fact that LiCl is easily soluble in alcohol, whilst LiOH is only sparingly soluble, as seen in the table:

	methanol	ethanol	isopropanol
LiOH	4.8g/l	1.8g/l	traceable
LiCl	400g/l	40g/l	20g/l

During the process the chloride ions of the corrosion are exchanged with hydroxide ions, and Lithium chloride is dissolved in the alcohols according to the process:

$$Li^{+}OH^{-} + Cl^{-} \longrightarrow Li^{+}Cl^{-} + OH^{-}$$

The hydroxide ions enter the metal and because of their greater size they seal off the metal and thus act as an inhibitor.

The method as practised in our lab After all the steps of investigation and documentation prior to the conservation process itself have been effected, the items of iron are mechanically cleaned as carefully as possible. Then the objects are totally dehydrated in a mixture of equal volumes of methanol and isopropanol under vigorous stirring and in repeated changes of liquid. Total dehydration is important, because even a small residue of water may invalidate the following processes.

Thereafter the objects are placed in equal volumes of pure, anhydrous methanol and isopropanol to which is added 2g of LiOH (analytic grade) per liter solution (delivered as a 33% solution in pure ethanol). The washing out of chlorides takes place under automatic stirring in a tightly sealed glass tank. It is continued until no change of the chloride concentration can be measured for days or weeks - the whole process tkaing from weeks to several months.

The objects are then impregnated in very much the same way as described for the items treated by the red-hot heating method. The mechanical cleaning, however, may vary considerably, from a light brushing to a long and difficult removing of corrosion.

We have deliberately refrained from entering into a discussion on when to use the two above-described methods, because the choice depends very much upon the nature of the objects to be conserved.

The great advantage of the Lithium hydroxide method is the much less violent physical and chemical treatment than is found with almost all other methods available for conserving iron. It is particularly advantageous to have done with the traditional washing out of chlorides etc. in aqueous solutions, which among other things leads to intercrystalline corrosion. This also means that it is possible to take samples for analysis even after conservation.

As a conclusion it can be said that generally speaking the Lithium hydroxide method is particularly suitable for little-corroded objects with fragile surface layers whereas the heating to redness procedure is an important method for very much corroded items of iron.

78/23/14

THE USE OF OXIDE FILMS TO PROTECT MONUMENTAL COPPER AND BRONZE SCULPTURE FROM ATMOSPHERIC CORROSION

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THE USE OF OXIDE FILMS TO PROTECT MONUMENTAL COPPER AND BRONZE SCULPTURE FROM ATMOSPHERIC CORROSION

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A comparative study of natural and artificial patinas and an analysis of practical work in conservation of antique outdoor coppers and bronzes show that natural patinas possess better protective properties, are more durable, less susceptible to atmospheric damages, and capable to preserve antique sculpture in dangerous environment. However, it is not always convenient to use natural patina as a protective coating either in the process of production or in the process of restoration. Thus, it takes a long time for patina to form on a metal surface, while exhibiting sculpture with its surface clean is not in line with the aesthetic tradition. At the first stage of patina formation, which lasts, depending on environmental conditions, from several months to several years, a thin oxide layer of little artistic value appears on the surface. The colour may be motley oxide tint with dark spots, uneven in hue, brilliance and transparency. Because the layer is very thin selective oxidation of some components of bronze, especially zink, often cannot be prevented. As a result, a light veil may appear on the surface and remain there for some time.

It is a world-spread practice to use artificial combined protective and decorative coatings both is sculpture production and restoration. The metal surface is chemically patinated, or else oxidated, after which it is coated with a protective layer of some organic material (wax, varnish or linseed oil). The choice of a technique is normally determined by aesthetic conside-

rations, such as desirable colour which is, for the most part, dark grey, black or brown. However, structure and properties of patina, to say nothing of the environment factor, are almost never taken into account.

Thin and porous coatings are extremely unstable under outdoor conditions and after the period of one to three years their destruction begins. Due to a complex arrangement of parts in a figure and different orientations of its surfaces in space the process of losing by organic films their protective properties and their subsequent transformation into natural patina takes rather an irregular course. On head, shoulders, south parts and some other places contrasting light grey, green or blue spots appear, while on unexposed surfaces dark artificial coatings may remain for decades.

In order to get rid of the spots and to improve aesthetic qualities of a figure old layers are periodically removed and replaced with new ones. The procedure is very expensive, besides, it inevitably leads to irrevertable mechanical and chemical wear of the surface; also, the relief and texture are smoothed and the original plastic forms of a figure are distorted at the expense of preserving its colour.

In USSR recently a new technique of protective and decorative coating of monumental bronzes and coppers has come into use. The metal surface is oxidated by methods that allow to obtain artificial films of cuprous oxide (but not of copper oxide and certainly not of copper sulfides), which resemble, in structure, composition physical and chemical and decorative properties, natural brown pating. By combining chemical and heat treatment it is possible to obtain films of sufficient density and thickness, which can be used without additional organic coatings - a fact of principal importance.

Cuprous oxide is a p-type semiconductor, that is an ionic compound with crystal lattice defects and deviations from the stochometric composition. The latter means that it contains copper in smaller amounts than required by the formula Cu_2O. Owing to that fact in some lattice paints there are defects in the form of cation vacancies. Positive charges that correspond to missing univalent cations are distributed among neighbouring cations which become bivalent. The lattice with a copper content lower than usual is near the film surface, contacting atmosphere. As it moves off from the surface approaching the junction between the film and metal vacancies are reduced in number and the lattice becomes a normal one. The varying oxide compositions at different film levels cause a concentration gradient which, together with lattice deficts, induces an intensive cation diffusion from the deep to the surface layers. The cation sourse is metal which, being ionized at the juncture, emits cations and electrons, the latter diffusing in the same direction and ionizing oxygen on the film surface. Copper cations and oxygen anions combine on the film or pore surface forming cuprous oxide. As a result self-packing and self-thickening of the film takes place. In thin parts where cations reach the surface sooner the film grows more rapidly which leads to a spontaneous increase of its uniformity.

Thus, thanks to lattice microdefect a cuprous oxide film can develop its protective properties in exploitation. However, concentration of cuprous oxide lattice defect and the induced cation diffusion depend on oxygen pressure on the film surface. If a film is coated with an organic substance which isolates it from environment there is practically no diffusion and protective properties of the film cannot be improved. It

follows thus that in order to realize the capacities of cuprous oxide films they should be used without additional protective coatings. This is also an indispensable condition for the second layer of basic cuprates (sulphites, carbonates, chlorides) to form on a film surface. The diffusion mechanism of two-layer patina formation is the same, though the rate of the formation is slower, owing to a lesser concentration of sulphur gases, carbon dioxide and water steam in air, as compared to oxygen concentration.

Because the principal agents in oxide film formation are atmosphere gases, aerosols, water steam and the wet films which appear on metal surface as a result of water condensation and absorption, natural pating forms, in the absence of organic coatings, rather evenly over the whole surface of a figure of a most complex configuration. Moreover, the formation of pating also takes place on unexposed objects, such as statues, reliefs, pillar hases and capitals in porticos, on belfry bells and in the cavities of a figure.

As the second layer of an oxide film forms on the surface the protective capacity of patina increases not only because of its thickening, but also because it becomes more corrosion resistant, due to the fact that basic salts are in a better dynamic and chemical equilibrum with environment them cuprous oxide.

Diffusion processess in patina are analogous to the process of metasomatosis in minerals, causing enlargement of particles and leading to structural uniformity. As a result, high-dispersed artificial films acquire dense and uniform micro-grouned structure in the course of their transformation in to natural patina. Their internal energy is reduced, as well as the thermal motion of particles, which means that an ion diffusion decreases, with the result that the formation of patina pro-

ceeds at a slower rate. As the process goes on the thermodynamic equilibrum of the metal-oxide film-basic cuprates-environment system is establish and the growth of patina practically ends.

Although quite simple, the oxidation technique with the formation of cuprous oxide, but without subsequent organic coating may be an efficacious solution of the problem of protective and decorative treatment of monumental coppers and bronzes. In clean rural and sea environment, unpolluted with industrial gases, patina growth is determined only by humidity. Having reached the maximum density and thickness of about 10-15 microns, a film remains unchanged at the stage of brown or black patina for decades and even centuries. In the case of sculpture conservation in industrial or sea-industrial environment artificial films should be regarded as intermediary coatings that must gradually transform into olive or blue patina. The rate of patina formation depends on concentration of active admixtures in air and humidity; the minimum time of the formation of a visible green layer is from 10 to 20 years.

The oxidation technique without organic coatings has some advantages over other methods of protective and decorative treatment of monumental coppers and bronzes. As distinct from the majority of mineral and organic coatings which eventually detiriorate, cuprous oxide films become more stable as time goes on. That organic protective coatings are not used saves money and scarce materials at the same time creating conditions for a uniform transformation of artificial oxide films into natural patinas. Oxidation of sculpture reduces the time of natural patina formation by several years, averts some undesirable side-effects and makes it possible to avoid exhibiting sculpture without a de-

corative coating. Oxidation of sculpture with subsequent one or two-layer patina formation allows to avoid constant replacement of coatings, saves money at the same time preventing sculpture from destruction and plastic detirioration. Finally, both primary oxide-films and two-layer patinas have a fine, mineral-like texture and beautiful colour. In this they differ considerably from black (or other dark) achromatic coatings on iron and some other materials, adding to the artistic originality and colour expressiveness of outdoor coppers and bronzes.

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